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<p>(54) Title: COMBINED SKIN MOISTURIZING AND CLEANSING BAR COMPOSITION</p>		
<p>(57) Abstract</p> <p>The present invention relates to a personal skin moisturizing and cleansing bar composition which comprises both a skin cleansing agent and a lipid moisturizing agent in the same bar which actually deposits an effective amount of the lipid on the skin of the user in the bath or shower. The bar composition of this invention comprises: (1) about 5 parts to about 40 parts of a lipid skin moisturizing agent; (2) about 10 parts to about 50 parts of a rigid crystalline skeleton network structure consisting essentially of selected fatty acid soap or a mixture of said soap and selected fatty acid; (3) about 1 part to about 50 parts of a lathering synthetic surfactant, and; (4) about 10 parts to about 50 parts water. The bar of the present invention can provide good cleansing, lather and good sensory feel and yet surprisingly provide a lipid moisturizing benefit via deposition of the lipid on the skin of the user. The bar composition is solid and on a macro scale is homogeneous.</p>		

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COMBINED SKIN MOISTURIZING AND CLEANSING BAR COMPOSITION

5 TECHNICAL FIELD

The present invention relates to personal skin moisturizing compositions and personal cleansing bar compositions.

BACKGROUND OF THE INVENTION

Moisturizers are usually applied directly to the skin as leave-on products.

10 Personal cleansing products are usually applied with water as a foam or lather and rinsed off with clear water. Ideal rinse off personal cleansers should cleanse the skin gently, causing little or no irritation without defatting and or drying the skin and without leaving skin taut after frequent use. Most lathering personal cleansing products, bar soaps, liquids and syndet bars fail in this respect.

15 Some current commercial personal cleansing bars claim to "moisturize" the skin. But, most of these current cleansing bar products do not deliver an adequate moisturizing benefit. Therefore, users typically must moisturize their skin with a separate leave-on product following cleansing.

It would be highly desirable to improve the delivery of skin moisturizers from a cleansing bar composition over the current commercial personal cleansing bars. If this were accomplished it would provide users with the convenience of obtaining both a cleansing and a moisturizing benefit from a single product.

Dual cleansing and lipid moisturizing bar compositions are very difficult to formulate and process. One reason is the cleansing ingredients, in general, tend to be incompatible with the lipid moisturizing ingredients. Another problem is processing, particularly, processing on a commercial scale, for they can be very sticky to process. Yet another problem is getting the lipid in the bar to deposit on the skin of the user. The deposition of lipid moisturizer from the bar, onto the skin can be very low due to loss of the lipid in the wash. Conversely, it can be too sticky if deposited on the skin. Still another problem is formulating a dual bar that lathers well. Another problem is formulating a dual bar that is hard and solid.

Needless to say, the actual deposition of lipid moisturizer from a lathering dual bar composition is essential for effective lipid benefit. No known prior art bar on the market today which claims to be a cleansing and lipid moisturizing bar, deposits as much as 3 micrograms of lipid moisturizer per cm. sq. of washed skin.

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In conclusion, there has been a need for a dual cleansing and lipid moisturizing bar composition: 1) which produces an abundant, stable, high quality lather, 2) which is an effective skin cleanser, 3) which is very mild to the skin and ocular mucosae, 4) which actually delivers an effective amount of a lipid moisturizing agent to the skin of the user during the wash; and 5) which is processable.

It is an object of the present invention to provide an effective, yet gentle, dual skin cleansing bar composition which actually deposit a lipid on the skin to provide a skin moisturizing benefit while maintaining its lathering, sensory and cleaning properties.

SUMMARY OF THE INVENTION

The present invention relates to a personal skin moisturizing and cleansing bar composition which comprises both a skin cleansing agent and a lipid moisturizing agent in the same bar which actually deposits an effective amount of the lipid on the skin of the user in the bath or shower.

The bar composition of this invention comprises: (1) about 5 parts to about 40 parts of a lipid skin moisturizing agent; (2) about 10 parts to about 50 parts of a rigid crystalline skeleton network structure consisting essentially of selected fatty acid soap or a mixture of said soap and selected fatty acid; (3) about 1 part to about 50 parts of a lathering synthetic surfactant, and; (4) about 10 parts to about 50 parts water.

The bar of the present invention can provide good cleansing, lather and good sensory feel and yet surprisingly provide a lipid moisturizing benefit via deposition of the lipid on the skin of the user. The bar composition is solid and on a macro scale is homogeneous.

BRIEF DESCRIPTION OF DRAWINGS

Figures 1-5 are photographs which show magnified views of samples of bars of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present bar is a lathering skin cleansing bar composition comprising by *weight parts of the following bar composition:*

- (a) from about 5 parts to about 40 parts of a lipid skin moisturizing agent, selected from the group of organic lipids, which are hydrophobic as defined by

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having a combined Vaughan Solubility Parameter (VSP) of from about 5 to less than about 10; and mixtures thereof;

- 5 ((b) from about 10 parts to about 50 parts of a rigid semi-continuous, interlocking open mesh crystalline network structure consisting essentially of fatty acid soap material selected from the group consisting of fatty acid soap and mixtures of said soap and fatty acid; wherein said fatty acid soap material has AT LEAST 75 % saturated alkyl chains; said alkyl chains being selected from the group consisting of chains of from 8 to 22 carbon atoms, and mixtures thereof; and wherein said soap and said fatty acid have a ratio of from 1:3 to 10,000:1;
- 10 c) from about 1 part to about 50 parts of a lathering synthetic surfactant having an equilibrium surface tension value of from 15 to 50 dynes per cm as measured at the CMC at 25°C; and
- d) from about 10 parts to about 50 parts water;
- 15 wherein said water and said lipid are predominantly within interstices of said open mesh crystalline network; wherein said bar composition has a Lipid Deposition Value of at least 3 microgram to about 1000 micrograms per sq. cm. of skin as measured by Lipid Deposition Protocol 1.

GLOSSARY OF TERMS AS USED HEREIN:

20 Vaughan Solubility Parameter (VSP) is a calculated parameter used to define a lipid's solubility. Vaughan parameters typically have a range of 5-25.

Lipid Deposition Value (LDV) is a measure of how much lipid is deposited on skin from compositions herein, the reading corresponds to the amount measured using a Sebumeter (typically the mean of six readings), as defined in Lipid Deposition Protocol 1, herein.

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Equilibrium Surface Tension is a measure of surface tension of a surfactant as measured at the critical micelle concentration at 25°C; units are dynes/cm.

Consistency, k , is a measure of lipid viscosity, used in combination with Shear index, to define viscosity for materials whose viscosity is a function of shear.

30 The measurements are made at 35°C and the units are poise (equal to 100 cps).

Shear index, n , is a measure of lipid viscosity, used in combination with Consistency, to define viscosity for materials whose viscosity is a function of shear. The measurements are made at 35°C and the units are dimensionless.

Elastic Modulus G' is used to define rheological properties of lipid and is a measurement of a lipids ability to store or return energy. The measurements are made at 35°C and the units are dynes/sq. cm.

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Viscous Modulus G'' is used to define rheological properties of lipid and is a measurement of unrecoverable energy. The measurements are made at 35°C and the units are dynes/sq. cm.

5 All parts, percentages and ratios used herein are by weight basis and all measurements are at 25°C, unless otherwise indicated.

DETAILED DESCRIPTION OF DRAWINGS

Figures 1-5 are photographs which show magnified views of samples of bars of the present invention. Cryo-Scanning Electron Microscopy (Cryo-SEM) sample preparation involves fracturing a shaped solid bar with simple pressure to obtain a fresh surface for examination. The fractured sample is reduced in size (razor blade)
10 to approximately 1 mm x 1 mm x 5 mm. The sample is then frozen in liquid nitrogen and then mounted and coated with a thin platinum layer. The Cryo-SEM used is a Model S-4100 Hitachi Field Emission Cryo-SEM.

Figure 1 shows a fractured cross section of soap bar (Example X) at 20,000
15 X magnification, focused on a non-lipid section of the bar.

Figure 2 shows a fractured cross section of soap bar (Example X) at 2,000 X magnification, focused on the lipid droplets in the bar (3 to 10 microns in size).

Figure 3 shows a fractured cross section of soap bar (Example X) at 100 X magnification.

20 Figure 4 shows a fractured cross section of soap bar (Example Y) at 5,000 X magnification, focused on the aqueous and lipid sections. The lipid is present as a lipid in water emulsion.

Figure 5 shows a fractured cross section of soap bar (Example Y) at 200 X magnification.

25 The following numbers identify elements and details of the Figures.

1. Fractured cross section of a preferred lipid soap bar Example X.
2. Shows a continuous aqueous phase at 20,000 X.
3. Shows crystalline soap fibers at 20,000 X.
4. Shows lipid droplets of 3 to 10 microns in diameter at 2,000 X.
- 30 5. Shows a continuous aqueous phase at 2,000 X.
6. Shows air pockets at 100 X.
7. Shows a typical section of fractured bar at 100 X, around air pocket; this area is further magnified in Figures 1 and 2.
8. Shows a pitted area at 5,000 X, which is a continuous aqueous phase
35 containing an emulsion.
9. Shows acyl Isethionate surfactant crystal platelets at 5,000 X.

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10. Shows lipid droplets at 5,000 X.
11. Shows air pockets at 200 X.
12. Is a lower magnification (200 X) of the section type shown in Figure 4.

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THE LIPID SKIN MOISTURIZING AGENT

The lipid skin moisturizing agent in the bar composition provides the skin of the user with a moisturization benefit via deposition of the lipid on skin during use. In this invention the lipid skin moisturizing agent is defined with scrutiny. The lipid type and its physical properties in this present invention hold the key to the overall product effectiveness, and is restricted to a hydrophobic material with the following defined physical and rheological properties.

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Vaughan Solubility Parameter Value (VSP)

The lipid in this present invention is further defined by its solubility parameter, as defined by Vaughan in Cosmetics and Toiletries, Vol. 103, p47-69, Oct. 1988. A lipid having a Vaughan Solubility Parameter Value (VSP) of from 5 to 10, preferably 6 to 9.5 or less than ten (10) is preferred for use in the bar compositions herein.

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VAUGHAN SOLUBILITY PARAMETER TABLE*

20	Cyclomethicone	5.92
	Squalene	6.03
	Petrolatum	7.33
	Isopropyl Palmitate	7.78
	Isopropyl Myristate	8.02
25	Castor Oil	8.90
	Cholesterol	9.55

* As reported in Solubility, Effects in Product, Package, Penetration and Preservation, C. D. Vaughan, Cosmetics and Toiletries, Vol. 103, October 1988.

Fatty acids, fatty acid soaps and water soluble polyols are specifically excluded from our definition of a lipid. Thus stearic acid, glycerine and propylene glycol are excluded from our definition of a lipid.

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SOME PREFERRED LIPIDS

Notwithstanding the rheological and solubility requirements, a wide variety of lipid type materials and mixtures of materials are suitable for use in the compositions of the present invention. Preferably, the lipid is selected from the group consisting of hydrocarbons oils and waxes, silicones, fatty acid derivatives,

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cholesterol, cholesterol derivatives, di and tri-glycerides, vegetable oils, vegetable oil derivatives, and acetoglyceride esters, alkyl esters, alkenyl esters, lanolin and its derivatives, milk -tri-glycerides, wax esters, beeswax derivatives, sterols and phospholipids mixtures thereof.

5 Hydrocarbon oils and waxes: Some examples are petrolatum, mineral oil micro-crystalline waxes, polyalkenes, paraffins, cerasin, ozokerite, polyethylene and perhydrosqualene.

Silicone Oils: Some examples are dimethicone copolyol, dimethylpolysiloxane, diethylpolysiloxane, high molecular weight dimethicone, mixed C1-C30 alkyl polysiloxane, phenyl dimethicone, dimethiconol, and mixtures thereof. More preferred are non-volatile silicones selected from dimethicone, dimethiconol, mixed C1-C30 alkyl polysiloxane, and mixtures thereof. Nonlimiting examples of silicones useful herein are described in U.S. Patent No. 5,011,681, to Ciotti et al., issued April 30, 1991, which is incorporated by reference.

10 Di and tri-glycerides: Some examples are castor oil, soy bean oil, derivatized soybean oils such as maleated soy bean oil, safflower oil, cotton seed oil, corn oil, walnut oil, peanut oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil and sesame oil, vegetable oils and vegetable oil derivatives; coconut oil and derivatized coconut oil, cottonseed oil and derivatized cottonseed oil, jojoba oil, cocoa butter, and the like.

20 Acetoglyceride esters are used and an example is acetylated monoglycerides.

Alkyl esters can be used and some examples are: isopropyl esters of fatty acids and long chain esters of long chain fatty acids, e.g. cetyl ricinoleate are especially useful herein. Some examples of these are isopropyl palmitate, isopropyl myristate, cetyl riconoleate and stearyl riconoleate. Other examples are: hexyl laurate, isohexyl laurate, myristyl myristate, isohexyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, diisopropyl adipate, diisohexyl adipate, dihexyldecyl adipate, diisopropyl sebacate, acyl isononanoate lauryl lactate, myristyl lactate and cetyl lactate.

25 Alkenyl esters are useful and some examples are oleyl myristate, oleyl stearate and oleyl oleate.

Lanolin and its derivatives are preferred and some examples are lanolin, lanolin oil, lanolin wax, lanolin alcohols, lanolin fatty acids, isopropyl lanolate,

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acetylated lanolin, acetylated lanolin alcohols, lanolin alcohol linoleate, lanolin alcohol riconoleate.

Milk glycerides are useful and an example is hydroxylated milk glyceride.

Polyol fatty acid polyesters are also useful.

5 Wax esters, such as beeswax and beeswax derivatives, spermaceti, myristyl myristate, stearyl stearate are also useful. Vegetable waxes are useful and some examples are carnauba and candelilla waxes. Sterols are useful and some examples are cholesterol, cholesterol fatty acid esters. Phospholipids, such as lecithin and derivatives, Sphingo lipids, ceramides, glycosphingo lipids are also useful.

10 It is more preferred when at least 70 % of the lipid is selected from the group consisting: petrolatum, mineral oil micro-crystalline waxes, paraffins, ozokerite, polyethylene, polybutene, polydecene and perhydrosqualene. dimethicones, cyclomethicones, alkyl siloxanes, polymethylsiloxanes and methylphenylpolysiloxanes, lanolin, lanolin oil, lanolin wax, lanolin alcohols, lanolin
15 fatty acids, isopropyl lanolate, acetylated lanolin, acetylated lanolin alcohols, lanolin alcohol linoleate, lanolin alcohol riconoleate castor oil, soy bean oil, maleated soy bean oil, safflower oil, cotton seed oil, corn oil, walnut oil, peanut oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil and sesame oil, and mixture thereof.

20 It is most preferred when at least 70 % of lipid is composed of lipids selected from the group consisting: petrolatum, mineral oil, paraffins, polyethylene, polybutene, polydecene, Dimethicones, alkyl siloxanes, cyclomethicones, lanolin, lanolin oil, lanolin wax. The remainder of the lipid is preferably selected from: isopropyl palmitate, cetyl riconoleate, octyl isononanoate, octyl palmitate, isocetyl stearate, hydroxylated milk glyceride and mixtures thereof.

25 The lipid is preferably in the bar as an emulsion having droplets ranging from about 0.1 microns to 100 microns, excluding anomalous very small or a few very large particles. While not being bound by any theory, particle size can impact the user perceived stickiness; with larger particles being perceived as more sticky. An example of a sticky lipid bar with large lipid particles is disclosed in allowed U.S.
30 Pat. Application Ser. No. 07/909,877, Kacher et al., filed July 7, 1992, incorporated herein by reference.

Pure petrolatum can be a sticky lipid and when used as the sole lipid in a 2-in-1 bar, it is preferred to have at least 75%, preferably 85%, of its particles smaller than 10 microns. However, when petrolatum is combined with other selected lipids the

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overall lipid stickiness can be reduced and the particle size for feel is less important and can range from 0.1 microns to 100 microns.

While not being bound by any theory, lipids outside of the rheology properties defined herein are either too easily emulsified and hence will not deposit, or are too "stiff" to adhere or deposit on to skin and provide a moisturization benefit. The lipid rheological properties are considered to have an important effect on lipid deposition. In addition, the rheological properties of the lipid are also important to user perception. Some lipids, on deposition to the skin, are considered too sticky and are not preferred by the user.

Lipid Rheological Table 1

<u>Range</u>	<u>k</u>	<u>n</u>	<u>G' at 1 Hz</u>	<u>G'' at 1 Hz</u>
	poise (1/sec) ⁿ⁻¹	(dimensionless)	(dynes/cm ²)	(dynes/cm ²)
Most preferred	50-2,000	0.20-.5	5,000-50,000	5,000-100,000
More Preferred	10-3,000	0.1-0.5	1,000-80,000	500-300,000
Preferred	5-5000	0.1-0.9	25-100,000	25-500,000

Two types of rheological parameters are used to define the lipid used herein. The viscosity of the fluid is represented by consistency (k) and shear index (n) and, while not being bound by any theory, is believed to represent the stickiness. The other type of parameter used herein, are the elastic modulus (G') and the viscous modulus (G''). While not being bound by any theory it is believed G' and G'' are important factors determining the lipid's emulsification characteristics.

The useful lipid herein has a shear index, n, of from about 0.1 to about 0.8 and a consistency, k, of: from 5 to 5,000 poise; preferably 10 to 3000 poise; more preferably 50 to 2,000 poise at 35° C. The preferred lipid rheology is further defined in the following table:

The shear index, n, and consistency, k, are well accepted industry standards for reporting the viscosity profile of a material that has a viscosity that is a function of the shear rate.

For all materials the viscosity, which is defined for instance in "Chemical Engineering, by Coulson and Richardson" is given by:

$$\text{Viscosity, } \mu = \sigma / \gamma'$$

Where σ is the shear stress, and γ' is the shear rate.

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The viscosity for all materials is measured by either applying a shear rate and measuring the resultant shear stress or vice versa.

- 5 The Carrimed CSL 100 Controlled Stress Rheometer is used to determine Shear Index, n , and Consistency, k , for the lipids herein. The determination is performed at 35°C with the 4 cm 2° cone measuring system typically set with a 51 micron gap and is performed via the programmed application of a shear stress (typically from about 0.06 dynes/sq. cm to about 5,000 dynes/sq. cm) over time. If
- 10 this stress results in a deformation of the sample, i.e. strain of the measuring geometry of at least 10⁻⁴ rad/sec, then this rate of strain is reported as a shear rate. These data are used to create a viscosity μ Vs. shear rate γ' flow curve for the material. This flow curve can then be modeled in order to provide a mathematical expression that describes the material's behavior within specific limits of shear stress
- 15 and shear rate. These results were fitted with the following well accepted power law model (see for instance: Chemical Engineering, by Coulson and Richardson, Pergamon, 1982 or Transport Phenomena by Bird, Stewart and Lightfoot, Wiley, 1960):

20 Viscosity, μ = $k (\gamma')^{n-1}$

Lipid Rheological Table 2

<u>Lipids</u>		<u>Consistency, k</u>	<u>shear index</u>	<u>G' at 1 HZ</u>	<u>G'' at 1 Hz</u>
Units		poise	n	dynes/sq. cm	dynes/sq. cm
5	Water	0.01	1.0		
	Microcrystalline Wax (MC)	**	**	**	**
	80 % Pet/20 % MC wax	3926-4822*	0.31-33*	306,400-621,000*	434,000-594,580*
	91 % Pet/9 % MC Wax	1983	0.15		
	Petrolatum	1080-1345	0.24	25,000-40,000	23,400-36,400
10	90 % Pet/10 % min oil	767-780	0.26		
	80 % Pet/20 % min oil	354-430	0.29-0.34	8,500-9300	6,700-7000
	60 % Pet/40 % min oil	111-115	0.42	1,000-2800	940-2500
	40 % Pet/60 % min oil	4.8-5.3	0.87	230-380	280
	Mineral (min) oil	0.81-0.82	1.0		
15	5 %SE/95 % min oil	1580-1787	0.16		
	95.9 %SBO/4.1 %MC wax	780-890	0.13-0.16		
	80 % Pet/20 % Polydecene	283-292	0.32-0.34	5881-7160	6118-6805
	65 % Pet/35 % Polydecene	115-120	0.4	1280-1407	1416-1446
	20 % Pet/80 % Polydecene	0.83	0.97-1.0	24.1	34.5
20	20 % SE/80 % Polydecene	1897-2035	0.19-0.22	1E6-1,370,000	280,000-980,000

* Measured with same instrument, but with 2 cm parallel plate geometry.

** Too stiff and solid to obtain readings

SE solid is a sucrose ester solid and is an example of a preferred polyol fatty acid polyester, SBO is soybean oil and Pet is petrolatum.

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Note that mineral oil, microcrystalline wax and some other lipids by themselves have rheological properties that are unsuitable for use in the present bar compositions; but may be blended with other lipids to provide acceptable lipid blends.

Test Protocol for determination of G' and G''

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The Carrimed CSL 100 Controlled Stress Rheometer is used to perform oscillatory tests at 35°C with the 4 cm 2° cone measuring system typically set with a 51 micron gap. The oscillatory tests at 35°C are carried out in 2 steps. The first step is a stress amplitude sweep at the expected starting and ending frequencies for the frequency sweep. These tests allow a determination to be made as to whether or not the test conditions are within the linear viscoelastic region for the test material

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over the anticipated frequency range. The linear viscoelastic region is a region

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where there is a linear relationship between stress and strain. The second step is a frequency sweep made at a stress level within that linear viscoelastic region. The frequency sweep allows the test material's viscoelastic behavior to be measured. The oscillatory test on a controlled stress rheometer is performed by applying a stress in an oscillatory manner and measuring the resulting oscillatory strain response and the phase shift between the applied stress wave form and the resulting strain wave form in the test material. The resulting complex modulus is expressed as a combination of the material's elastic (G') and viscous (G'') components:

The elastic modulus G' is a measure of a materials ability to store recoverable energy. This energy storage can be the result of the ability of a complex polymer, structural network, or a combination of these to recover stored energy after a deformation. The viscous or loss modulus G'' is a measure of the unrecoverable energy which has been lost due to viscous flow.

The lipid is present in the bar at a level of from about 5 parts to about 40 parts by weight of the bar. Its more preferred levels are 10 parts to 40 parts; and 10 parts to 30 parts. The most preferred lipid levels are from about 12 or 15 parts to about 25 parts.

Known market bars contain little or no lipid. Known market bars that contain lipid deposit lipid at an efficiency of less than 3 microgram per sq. cm. of skin as measured by Deposition Protocol 1.

The lipid in this present invention is deposited on skin during use at an efficiency that produces at least 3 μg of lipid per sq. cm of skin. The preferred level of deposition is from about 5 $\mu\text{g}/\text{sq. cm}$ to about 1000 $\mu\text{g}/\text{sq. cm}$. The more preferred levels are from 5 or 10 $\mu\text{g}/\text{sq. cm}$ to about 500 $\mu\text{g}/\text{sq. cm}$ and 25 $\mu\text{g}/\text{sq. cm}$ to about 500 $\mu\text{g}/\text{sq. cm}$, as measured by lipid Deposition Protocol 1. It has been found that a certain minimum level of lipid is required in order to get any measurable deposition of the lipid on skin.

LIPID DEPOSITION VALUE

The level of lipid deposition on skin can be measured by different protocols, all are modeled after how skin cleansing products are typically used by consumers. All the protocols are "in vivo", and all tests are made using a statistically designed protocol using at least 6 subjects per prototype.

All protocols consist of a common exaggerated product application stage followed by a determination of the deposited lipid amount. The following two protocols only differ in the analytical technique used to quantify the amount of deposited lipid on the skin. The quantification of lipid is "in vivo" and as such has a wide variance due to differences in skin type and condition. To offset this a

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balanced design is used to test prototypes; balanced in skin type and using a large base size. In all cases product application and measurement is undertaken by a trained technician to reduce variability.

Prep For Lipid Deposition For Protocols 1 & 2

- 5 The subject wets the entire surface of the inner forearm with 95-100°F (35° C-38°C) water. The technician using exam gloves, wets the appropriate bar with tap water and then rotates the bar in both hands for (10) seconds to generate lather. The technician then rubs the bar on the inner forearm from the wrist to the elbow and back down again for 20 seconds (i.e., exactly 20 rubs up and 20 rubs down).
- 10 The bar is then set aside and the subject's forearm is rubbed by the technician for ten seconds by rubbing the gloved hand up and down the subject's inner forearm, again from elbow to wrist. The lather is allowed to remain on the forearm for fifteen seconds, followed by a thorough rinse for fifteen seconds. After rinse, the technician gently pats the forearm dry with a disposable paper towel. The process
- 15 is repeated two more times for a total of three washes.

LIPID DEPOSITION PROTOCOL 1

- The unit used is a Sebumeter SM810 which is commercially available from Courage and Khazaka GmbH and is reported to be recognized by the scientific world. The Sebumeter measures lipid on the skin via photometry of a special
- 20 plastic strip, which becomes transparent when it absorbs lipids. The plastic strip is extended over a mirror which is connected to a spring. The measuring head of the device (comprised of spring, mirror and plastic strip) is pressed against the skin for 30 seconds. The value ($\mu\text{g/sq. cm}$) is indicative of the amount of lipid on the skin, and increases with increased amount of lipid. The method is insensitive to
- 25 humidity. Six Sebumeter readings are taken along the length of the forearm and the Lipid Deposition Value, LDV, ($\mu\text{g/sq. cm}$) is defined as the mean of the six readings.

 The Sebumeter has the following limitations:

1. The Sebumeter tape also detects natural skin lipids. A criterion of this test
- 30 was that subjects baseline value measured on the Sebumeter, prior to washing, be less than or equal to 1 or 2 $\mu\text{g/sq. cm}$ of forearm skin.
2. The Sebumeter like other surface extraction measurements may not measure all the deposited lipid, if the skin topography is undulating it is possible that deposited lipid may not be extracted by the Sebumeter tape.

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3. The Sebumeter tape becomes saturated at a LDV of above about 300 $\mu\text{g}/\text{sq. cm}$; so it is understood that for deposition values above 300 $\mu\text{g}/\text{sq. cm}$, Protocol 2 is used.

LIPID DEPOSITION PROTOCOL 2

5 The second protocol uses a solvent extraction method similar in type to that described in the Journal Society of Cosmetic Chemists of Great Britain Vol. 21 (p 521-532), 1970. An extraction cup is firmly attached to the forearm and heptane poured in to the cup, such that it is in contact with the forearm. The solvent extract containing the extracted lipid is analyzed by standard gas chromatographic
10 methods.

LIPID DEPOSITION VALUE CONVERSION

Lipid Deposition Values, LDV, (as defined by the mean of six Sebumeter Readings using Protocol 1) may be converted into actual deposition of lipid on skin. This conversion factor is dependent on lipid type. For example, a petrolatum
15 deposition of about 5 $\mu\text{g}/\text{sq. cm}$ for Protocol 2 is equal to a Sebumeter Lipid Deposition Value of about 2 $\mu\text{g}/\text{sq. cm}$ and a petrolatum deposition of about 90 $\mu\text{g}/\text{sq. cm}$ for Protocol 2 is equal to a Sebumeter Lipid Deposition Value of about 52 $\mu\text{g}/\text{sq. cm}$.

THE RIGID CRYSTALLINE NETWORK STRUCTURE

20 The rigid crystalline network structure is a crystalline skeleton structure comprising a rigid interlocking, open, three-dimensional mesh which consists essentially of the selected fatty acid soap material. A mixture of said soap and selected fatty acid is preferred. The crystalline network can comprise crystals in the form of either interlocking platelets and/or fibers, preferably fibers. Preferably said
25 fibers are composed of sodium and magnesium soap and most preferable sodium soap. The interlocking mesh can impart strength to the three-dimensional structure, even in the presence of relatively high levels of lipid and water; and even when the bar is allowed to soak overnight in water.

Once formed, a bar (shaped solid) comprising the rigid skeletal structure of
30 the present invention loses its rigidity when subjected to fracturing mechanical forces, e.g., those used in a conventional plodded bar making process as disclosed in U.S. Pat. No. 4,812,253, Small et al., or U.S. Pat. No. 4,820,447, Medcalf et al. While not being bound to any theory, it is theorized that this is because the fracturing mechanical forces shear and break up the rigid, skeletal structure into

smaller pieces. Thus, when a bar composition of the present invention is flaked or the finished bar sheared in a plodder, a much softer bar results.

On the other hand, when a finished conventional bar is plodded or replodded, the replodded conventional milled bar or freezer bar is still very hard.

5 The skeletal structure contains substantial "void" areas which are filled by a two phase lipid and aqueous emulsion, preferably an oil in water emulsion. The presence of said rigid crystalline structure is believed to be a necessary, but not the only condition for lipid deposition from a 2-in-1 bar. Some bars which contain lipid in their formulation and which have rigid crystalline structure, do not deposit
10 at least 3 μg of lipid per sq. cm of skin tested using Lipid Deposition Protocol 1. One such bar is made by a freezer process as disclosed in US Pat. Application Serial No. 08/037,479, to Taneri et al., incorporated herein by reference, and is distinguished from the bars of this invention.

15 It is a surprising aspect of this invention that a substantial level of lipid and water, which can form an oil in water emulsion, can be incorporated into a solid bar without having a significant negative impact on the physical properties of the bar, such as bar hardness, lather and smear; and that said bar can deposit at least 3 μg of lipid, per square centimeter of skin, as measured using Lipid Deposition Protocol 1. In conventional bars, high levels of water and lipid can impact the overall bar
20 physical properties because the components either modify the phase and structure of the soap or synthetic surfactant components that primarily determine the bar's physical properties. The combination of two or more phases (e.g., soap and aqueous solution) drastically changes the colloidal structure, and consequently, the physical properties and processability of a conventional bar.

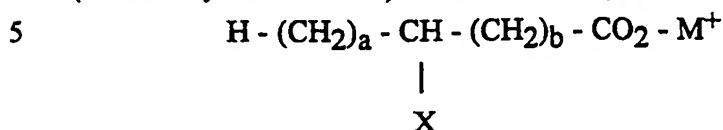
25 Thus, conventional bars are more limited in the type, levels and composition of materials that can be incorporated into the bar than the present invention.

30 The soap (neutralized carboxylic acid) is selected from the group consisting of: sodium soap, magnesium soap and sodium di-carboxylic acid; and mixtures thereof. The monocarboxylic acid has a fatty alkyl chain of from about 8 to about 24 carbon atoms and the di-carboxylic acid has a fatty alkyl chain of from about 12 to about 18 carbon atoms. The more preferred fatty acid soap material is defined herein as a material selected from the group consisting of monocarboxylic fatty acid soap and mixtures of said soap and monocarboxylic fatty acid; wherein fatty acid soap material is at least 80 % saturated and has an alkyl chain of from 8
35 to 22 carbon atoms, and mixtures thereof. The most preferred fatty acid material is essentially saturated fatty acid alkyl chains of from 8 to 22 carbon atoms with at least 75 % of it having a chain length of from 10 to 18; preferably 12 to 18 carbon

- 15 -

atoms and of which at least about 25 %, and most preferably 50 % of said saturated fatty alkyl chains have 12 to 14 carbon atoms.

In other words, at least 80 %, preferably 90 %, of the monocarboxylic acid (of the fatty acid material) has the following general formula:



wherein:

$$a + b = 8 \text{ to } 20$$

$$\text{each } a, b = 0 \text{ to } 20$$

$\text{X} = \text{H}, \text{OR}, \text{O-CO-R}, \text{R}, \text{ or mixtures thereof}$

$\text{R} = \text{C1-C3 alkyl}, \text{H}, \text{ or mixtures thereof}$

$\text{M} = \text{Na}, (\frac{1}{2}\text{Mg}), \text{ or mixtures thereof.}$

The above cleansing bar is more preferred when said $a + b = 10-16$; each of said $a, b = 0-16$; said $\text{X} = \text{H}, \text{OR}; \text{R} = \text{H};$ and $\text{M} = \text{Na}$. Examples of the most preferred fatty acids are: lauric acid, myristic acid, palmitic acid, stearic acid and 12-hydroxystearic acid.

The fatty acid soap material of the present invention comprises about 10 parts to about 50 parts by weight of the bar. Some preferred levels of fatty acid soap material are from about 15 parts to 35 parts and from about 15 parts to 25 parts *by weight of the bar*.

A bar is preferred when the fatty acid soap material is sodium and magnesium fatty acid soap, and is highly preferred when no more than 25 % is magnesium soap.

Some preferred ratios of said unneutralized (free) carboxylic acid to soap is from about 3:1 to all soap, and from about 1:2 to all soap, and a most preferred ratio is from about 1:4 to 1:10,000. Some other ratio examples are: 3:1, 1:10 and 1:200.

The following Table set out some levels and preferred properties of said fatty acid soap material which forms said rigid crystalline network structure.

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Fatty Acid Soap Material Table

	Broad	Preferred	Most
preferred			
Fatty Acid Soap parts	10-50 parts	15-35 parts	15-25 parts
5 Chain Length	8-24	8-22	12-18
% saturated	75 %	80 %	90 %
Minimum ratio of			
Soap:Fatty Acid*	1:3	2:1	4:1

*All soap bars can be made with little or no free fatty acid.

10

THE LATHERING SYNTHETIC SURFACTANT

The bar composition comprises a lathering synthetic surfactant selected from the group consisting of anionic surfactants; nonionic surfactants, cationic surfactants, amphoteric surfactants, and mixtures thereof.

15

The lathering synthetic surfactant is defined herein as a synthetic surfactant or mixes thereof that when combined have an equilibrium surface tension of between 15 and 50 dynes/cm, more preferably between 20 and 45 dynes/cm as measured at the CMC (critical micelle concentration) at 25°C. Some surfactant mixes can have a surface tension lower than those of its individual components.

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TABLE OF SOME SYNTHETIC SURFACTANTS SURFACE TENSION*

<u>Surfactant</u> (dynes/cm)		Surface tension at CMC
Anionics		
5	Sodium Dodecane Sulfonate	43
	Potassium Dodecane Sulfonate	38
	Sodium Dodecyl Sulfate	40
	Sodium Tetradecyl Sulfate	35
	Sodium hexadecyl Sulfate	37
10	Sodium Dodeceth-2 Sulfate	42
	Sodium Decyl Benzene Sulfonate	48
	Sodium Dodecyl Benzene Sulfonate	47
	Sodium Hexadecyl Benzene Sulfonate	45
15	Cationics	
	Tetradecyl Trimethyl Ammonium Bromide	41
	Dodecyl Trimethyl Ammonium Methane Sulfonate	39
	Zwitterionics	
20	Dodecyl Betaine	33
	Hexadecyl Betaine	35
	Dodecyl Benzyl methyl Ampho Acetate	33
	Nonionics	
25	1,2 Dodecyldiol	23
	1,3 Pentadecyldiol	27
	Hexeth-6	32
	Deceth-6	30
	Dodeceth-3	28
30	Dodeceth-12	40
	Hexadeceth-6	32
	Hexadeceth-21	45
	Nonoxynol-10	31
	Nonoxynol-30	41
35	Dimethicone copolyol	21-22

* As calculated from Surfactants and Interfacial Phenomena by Rosen, Wiley, 1988)

TABLE OF SOME PREFERRED SURFACTANTS SURFACE TENSION**

<u>Surfactant</u>	<u>Surface tension (dynes/cm)</u>
C12-C14 Glycerylether sulfonate	47
Sodium Lauryl Isethionate	42
5 Sodium Coco Isethionate	42
Sodium Stearyl Isethionate	72
Sodium Ether (3) Sulphate	47
Sodium Coco Taurate	43
Sodium Lauryl Sarcosinate	42

10

**Measured on Kruss BP-10 Dynamic surface tensiometer, these measurements were not equilibrium, nor at the CMC.

Equilibrium measurements are typically lower than Dynamic. .

15 The combined personal cleansing and moisturizing bar composition herein comprises at least from about 0.5 or 1 part to about 50 parts, preferably from about 5 parts to about 40 parts, and most preferably from about 10 parts to about 35 parts of a lathering synthetic surfactant.

20 Anionic surfactants useful herein include acyl isethionates, acyl sarcosinates, alkylglycerylether sulfonates, methylacyl taurates, paraffin sulfonates, linear alkyl benzene sulfonates, N-acyl glutamates, alkyl sulfosuccinates, alpha sulfo fatty acid esters, alkyl ether carboxylates, alkyl phosphate esters, ethoxylated alkyl phosphate esters, alpha olefin sulphonate, the alkyl ether sulfates (with 1 to 12 ethoxy groups), and mixtures thereof, wherein said surfactants contain C8 to C22 alkyl chain. The anionic surfactant is more preferred at about 8 parts to about 30 parts, selected from the group consisting of acyl isethionate, acyl sarcosinates, alkyl sulfosuccinates, alkylglycerylether sulfonates, methylacyl taurates, alkyl ether sulfates, alkyl sulfates, alkyl phosphate esters and mixtures thereof, wherein said surfactants contain C8 to C18 alkyl chains and wherein the counterion is selected from the group consisting of : Na, K, NH₄, N(CH₂CH₂OH)₃.

30 Amphoteric synthetic surfactants cannot serve as the sole surfactant in this product, but are preferred as a co-surfactant at a lower level of from about 1 part to about 10 parts, by weight and the more preferred types are selected from alkyl-ampho mono- and di-acetates, alkyl betaines, alkyl sultaines, alkyl amidopropyl betaines, alkyl amidopropyl hydroxysultaines, and mixtures thereof, wherein said surfactants contain C8 to C22 alkyl chains.

35 Nonionic synthetic surfactant cannot serve as the sole surfactant in this product, but can be used as a co-surfactant at a lower level of from about 3 parts to

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about 17 parts, by weight. The more preferred types selected from the group consisting: alkyl glucose amides, alkyl glucose esters, polyoxyethylene amides, fatty alkane amides, alkyl amine oxides, alkyl polyglucosides, polyoxy ethylene alkyl phenols, polyoxyethylene esters of fatty acids, EO/PO block co-polymers such as
5 polyoxamines and poloxamers, sorbitan esters and alcohol esters, and mixtures thereof.

Cationic synthetic surfactant cannot serve as the sole surfactant in this product, but are preferred as a co-surfactant at a lower level of from about 0.5 parts to about 6 parts, by weight. The more preferred types of cationic surfactants
10 are selected from the group consisting: alkyl trimonium chloride and methosulfate, and dialkyldimonium chloride and methyl sulphate, and alkyl alkonium chloride and methyl sulphate and mixtures thereof. These surfactants contain C12 to C24 carbon atoms per alkyl chain. The most preferred cationic is selected from the group consisting of stearylkonium chloride, stearyltrimonium chloride, Di-stearyl-
15 dimonium chloride, and mixtures thereof.

Cationic surfactants may also act as a lipid deposition aid and thus a preferred lathering skin cleansing bar composition comprising by *weight parts of the bar composition*:

- (a) from about 10 parts to about 50 parts of a rigid semi-continuous, interlocking
20 open mesh crystalline network structure consisting essentially of a fatty acid soap material selected from the group consisting of fatty acid soap has at least 75% saturated alkyl chains; said alkyl chains being selected from the group consisting of chains of from 8 to 22 carbon atoms, and mixtures thereof; and;
- (b) from about 3 parts to about 40 parts of a lipid skin moisturizing agent,
25 selected from the group of organic lipids, which are hydrophobic as defined by having a Vaughan Solubility Parameter (VSP) of from about 5 to less than about 10; and mixtures thereof;
- (c) from about 1 part to about 50 parts of a lathering synthetic surfactant; and
- (d) from about 10 parts to about 50 parts water;
- (e) from about 0.5 to about to about 6 parts of a cationic surfactant; and
30 wherein said water and said lipid are predominantly within interstices of said open mesh crystalline network; wherein said bar composition has a Lipid Deposition Value of at least 3 microgram to about 1000 micrograms per sq. cm. of skin as measured by Lipid Deposition Protocol 1; and wherein said cationic surfactant
35 improves the Lipid Deposition Value.

WATER AND THE AQUEOUS PHASE

The moisturizing and cleansing bar compositions of the present invention comprise water as an essential component. The water is present at a level of from about 10 parts to about 50 parts, preferably from about 12 parts to about 45 parts, and most preferably from about 15 to about 35 parts. A substantial percentage of the water forms the key part of an aqueous phase, which may also contain other water soluble components. Polyols and surfactants are water soluble.

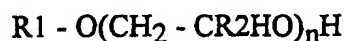
While not being bound to any theory, the presence of a lipid in water emulsion is believed to be important to lipid deposition on the skin. The level of water is key to forming a lipid in water emulsion. Thus, an effective amount of water is required to form an aqueous phase to support the lipid in water emulsion. The level of aqueous phase to lipid is preferably greater than 1:1, e.g., 2:1.

While not being bound to any theory, the interlocking crystalline network physically entraps the lipid in water emulsion, preventing phase separation of the lipid. On lathering the emulsion is released. It has also been found that bars of the compositions herein, produce a lipid in water emulsion in its lather. This emulsion in the lather is unstable and deposits lipid on the skin during the wash cycle.

The upper range of water is adjusted to provide a desired bar hardness and bar composition stability. Also enough water is required to properly process the bar, so the lower amount of water is restricted by an ability to pour the mix, comprising the final bar composition, into molds at the pour temperature and yet provide a bar which provides lipid deposition.

Optional Ingredients

A highly preferred optional component of the present compositions are one or more humectants and solutes. A variety of humectants and solutes can be employed and can be present at a level of from about 0.1 % to about 50 %, more preferably from about 0.5 % to about 35 %, and most preferably from about 2 % to about 20 %. of a non-volatile, organic material having a solubility of a least 5 parts in 10 parts water. A preferred water soluble, organic material is selected from the group consisting of a polyol of the structure:



where R1 = H, C1-C4 alkyl; R2 = H, CH₃ and n = 1 - 200; C2-C10 alkane diols; guanidine; glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium); lactic acid and lactate salts (e.g. ammonium and quaternary alkyl ammonium); polyhydroxy alcohols such as sorbitol, glycerol, hexanetriol, propylene

glycol, hexylene glycol and the like; polyethylene glycol; sugars and starches; sugar and starch derivatives (e.g. alkoxylated glucose); panthenol (including D-, L-, and the D,L- forms); pyrrolidone carboxylic acid; hyaluronic acid; lactamide monoethanolamine; acetamide monoethanolamine; urea; and ethanol amines of the
5 general structure $(\text{HOCH}_2\text{CH}_2)_x\text{NH}_y$ where $x = 1-3$; $y = 0-2$, and $x+y = 3$, and mixtures thereof. The most preferred polyols are selected from the group consisting of glycerine, polyoxypropylene(1) glycerol and polyoxypropylene(3) glycerol, sorbitol, butylene glycol, propylene glycol, sucrose, urea and triethanol amine.

Polyols may also act as a lipid deposition aid and a preferred lathering skin
10 cleansing bar composition comprising by *weight parts of the bar composition*:

- (a) from about 10 parts to about 50 parts of a rigid semi-continuous, interlocking open mesh crystalline network structure consisting essentially of a fatty acid soap material selected from the group consisting of fatty acid soap has at least 75% saturated alkyl chains; said alkyl chains being selected from the group
15 consisting of chains of from 8 to 22 carbon atoms, and mixtures thereof; and;
- (b) from about 3 parts to about 40 parts of a lipid skin moisturizing agent, selected from the group of organic lipids, which are hydrophobic as defined by having a Vaughan Solubility Parameter (VSP) of from about 5 to less than about 10; and mixtures thereof;
- 20 (c) from about 1 part to about 50 parts of a lathering synthetic surfactant; and
- (d) from about 10 parts to about 50 parts water;
- (e) from about 0.5 to about 35 parts water soluble polyol.

wherein said water soluble organic material is at least 50 % soluble in water; and wherein said water and said lipid are predominantly within interstices of said open
25 mesh crystalline network; wherein said bar composition has a Lipid Deposition Value of at least 3 micrograms to about 1000 micrograms per sq. cm. of skin as measured by Lipid Deposition Protocol 1. The polyol is used at a preferred level which improves the Lipid Deposition Value.

The above lathering skin cleansing bar composition is preferred when said
30 water soluble organic material is from about 3 parts to about 20 parts, by weight of said bar; and wherein said organic material is selected from the group consisting of glycerine, polyoxypropylene (1) glycerol and polyoxypropylene (3) glycerol, sorbitol, butylene glycol, propylene glycol, sucrose, and urea and triethanolamine; and wherein said lipid is from about 15 parts to about 25 parts, by weight of the
35 bar; and wherein said synthetic surfactant is from about 15 to about 30 parts by weight of the bar; said soap is present at a level from about 15 parts to about 25 parts and said soap is essentially C-12-18 carboxylic acids, with at least 50 % being

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C12 or C14; and wherein at least 75 % of said lipid by weight of said lipid is selected from the group consisting: petrolatum, micro crystalline wax, mineral oil or polydecene and mixes thereof; and wherein 5 to 25 % of said lipid by weight of said lipid is selected from the group consisting: dimethicone or alkyl polysiloxane.

5 The use of oil thickening polymers, such as those listed in EP 0 547 897 A2 to Hewitt, published 23/06/93, incorporated herein by reference, are useful if the final rheology of lipid and polymer falls within the preferred range.

10 A preferred optional ingredient are one or more cationic and/or nonionic polymeric skin conditioning agents. A variety of polymers can be employed and can be present at a level of from about 0.1 parts to about 10 parts, and more preferably 0.25 parts to about 3 parts of a polymeric, nonionic, cationic or hydrophobically modified polymeric skin feel aid, selected from the group consisting of cationic polysaccharides of the cationic guar gum class with molecular weights of 1,000 to 3,000,000, cationic and nonionic homopolymers derived from
15 acrylic and/or methacrylic acid, cationic and nonionic cellulose resins; cationic copolymers of dimethyldialkylammonium chloride and acrylic acid; cationic homopolymers of dimethyldialkylammonium chloride; cationic polyalkylene and ethoxypolyalkylene imines; and mixes thereof. Examples are hydroxypropyl guar, guar hydroxypropyltrimonium chloride, polyquaternary 3, 5, 6, 7, 10, 11 and 24. In
20 order to achieve the benefits described in this invention, the polymer must have characteristics, either structural or physical which allow it to be suitably and fully hydrated and subsequently well incorporated into the soap matrix.

Other Optional Components

25 A variety of additional ingredients can be incorporated into the compositions of the present invention. These materials including, but not limited to, bar appearance aids, salts and their hydrates, clays, and other "filler materials" are listed in US Pat. Application Serial No. 07/782,956 to Kacher et al, incorporated herein by reference. Examples of other suitable materials are disclosed in U.S. Patent No. 4,919,934, to Deckner et al., issued April 24, 1990; which is incorporated herein by
30 reference.

Other non limiting examples of these additional ingredients include vitamins and derivatives thereof (e.g., ascorbic acid, vitamin E, tocopheryl acetate, and the like); sunscreens; thickening agents (e.g., polyol alkoxy ester, available as Crothix from Croda); preservatives for maintaining the anti microbial integrity of the
35 compositions; anti-acne medicaments (resorcinol, salicylic acid, and the like); antioxidants; skin soothing and healing agents such as aloe vera extract, allantoin

and the like; chelators and sequestrants; and agents suitable for aesthetic purposes such as fragrances, essential oils, skin sensates, pigments, pearlescent agents (e.g., mica and titanium dioxide), lakes, colorings, and the like (e.g., clove oil, menthol, camphor, eucalyptus oil, and eugenol).

5 More preferably the composition will include from about 0.1 to about 50 % of other ingredients selected from the group consisting of:

- from about 0.5 to about 5 parts potassium soap;
- from about 0.5 to about 5 parts alkoxylated ammonium and/or alkylammonium and/or alkoxylated aliphatic amines and/or polyethoxylated amine soap;
- 10 • from about 0.5 to about 15 parts calcium soap;
- from about 0.5 to about 50 parts of impalpable water insoluble materials selected from the group consisting of calcium carbonate and talc;
- from about 0.5 to about 25 parts of aluminosilicate clay and/or other clays; wherein said aluminosilicates and clays are selected from the group consisting of
- 15 zeolites, kaolin, kaolinite, bentonite, halloysite, calcined clays, montmorillonite, illite and attapulgite.
- from about 0.5 to about 25 parts dextrin, corn and wheat starch;
- from about 0.1 to about 15 parts of salt and salt hydrates; and mixtures thereof; and wherein said salt and salt hydrate have a cation selected from the group
- 20 consisting of: sodium, potassium, magnesium, calcium, aluminum, lithium ammonium, alkoxylated ammonium, alkylammonium, alkoxylated aliphatic amines, polyethoxylated amines; and wherein said salt and/or salt hydrate have an anion selected from the group consisting of: chloride, sulfate, isethionate, bromide, metasilicate, orthophosphate, pyrophosphate, polyphosphate,
- 25 metaborate, tetraborate, carbonate, bicarbonate, hydrogen phosphate, methyl sulfate, and mono- and polycarboxylate of 1 to 6 carbon atoms or less;
- from about 0.1 to about 1 parts whitening aid;
- from about 0.1 to about 2 parts of a fragrance or perfume;
- from about 0.1 to about 5 parts of a chelant, preserve or anti fungal/anti
- 30 microbial/bacterial agent.

Non limiting examples of suitable carboxylic copolymers, emulsifiers, emollients, and other additional ingredients are disclosed in U.S. Patent No., 5,011,681, to Ciotti et al., issued April 30, 1991, which is incorporated by reference herein.

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THE BAR COMPOSITION

As described above, the bar dual composition of this invention can provide good cleansing and foaming and yet moisturize the skin via lipid deposition. The bar composition of this invention itself has a Lipid Deposition Value (LDV) of at least 3 micrograms per sq. cm. This means that it will deposit at least 3 micrograms of lipid on a sq. cm of forearm skin using Lipid Deposition Protocol 1 disclosed herein.

While not being bound to any theory, the presence of an unstable lipid in water emulsion in the lather is believed to be key to deposition of lipid on the skin during the wash cycle.

Two-in-One Bar Lipid Stability Centrifuge Test

The following test is used to determine the degree of stability of the lipid in a 2-in-1 (dual) bar composition. A ten percent (10 %) solution of the bar is made by weighing 10 grams of the bar, finely chopped, to 120°F (49 C) city water. It is stirred overnight (18 hours) using a magnetic stir plate and 1/2" stir bar.

The stirred sample is then centrifuged for 150 minutes at 10,000 RPM and 25°C using a Beckman L8-80-R60 Ultracentrifuge with a SW-40 rotor. If the lipid in water emulsion is suitably unstable, a lipid top layer is observed.

Such a sample prepared from a bar (Example B herein) of this invention has a 1 mm sticky white top lipid layer, a 74 mm layer of clear liquid and a 1 mm white solid bottom layer.

An IR scan of the top layer shows the composition to be predominately petrolatum, with traces of water, sodium coco isethionate and glycerine present, confirming the emulsion model.

No known commercially available prior art bar which contains a lipid has a measurable quantity of lipid on the top layer, when subjected to the above test.

The dual moisturizing and cleansing bar of this invention can be made by either of the following processes:

A BATCH PROCESS

1. Fatty acid precursor(s) and polyol if used are heated to 70°C,
2. A salt, water (excluding water coming in with other raw materials) and caustic solution (50 % sodium hydroxide) are added and the mixture is stirred at a slow speed until smooth forming an aqueous molten liquid. The temperature during neutralization of the molten liquid increases to ~95°C.
3. The following ingredients are added preferably in the following order and the temperature is maintained at ~85°C: synthetic surfactant,

- 25 -

preservatives (if any), whitening aid (if any) and some sensory aid, such as silicones. Perfume is the penultimate ingredient.

4. The pre-heated lipid, is added last and mixed for about two minutes on low speed. The temperature is maintained at about 85°C. the duration and intensity of the mix post lipid is considered important. If mixed too long or too little or too intense the bar quality or lipid deposition suffers. The goal is to create a uniform mix with lipid emulsion properties that yield bars which have lipid depositions values of from 2 to 500 micrograms per square centimeter.
5. The molten liquid mixture is poured into shaped molds. The molten liquid crystallizes (solidifies) on cooling to room temperature and the resultant bars are removed from the molds.

AN IN-LINE MIXING PROCESS

1. Fatty acid precursor(s) and optionally polyol are heated to about 70°C in Mixing Vessel 1,
2. A salt, water (excluding water coming in with other raw materials) and caustic solution (50 % sodium hydroxide) are added and the mixture is stirred at a slow speed until a smooth aqueous molten liquid is formed. The temperature during neutralization of the molten liquid increases to about 95°C.
3. Other ingredients are added preferably in the following order and the temperature is maintained at ~85°C: synthetic surfactant, preservatives (if any), whitening aid (if any) and some sensory aid, such as silicones. Perfume is the penultimate ingredient.
4. The lipid is pre-heated to about 70-75°C in a separate Mixing Vessel 2
5. The material from Mixing Vessels 1 and 2 are pumped and metered together at pre-determined rates designed to yield the final composition. The combined stream passes through a cooling and agitating device unit (freezer) as described in US Patent No. 2,295,594, to Mills, issued Sept. 15, 1942 and 3,835,058 to White, issued Sept. 10 1974. which provides both partial cooling and mixing. Cooling in the present process is optional and must be limited. A pourable temperature is maintained and the duration and intensity of the mix for this step is considered very important. If mixed too long or too little or too intense the pourability of the mix or the bar quality or the bar lipid deposition suffer. The goal is to create a uniform and

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pourable mix which has only semi-stable lipid emulsion properties and yield bars which are uniform and have lipid depositions values of from about 3 to 500 micrograms per square centimeter.

- 5 6. The uniform and pourable mixture exits the freezer via a nozzle and flows into bar shaped molds. The mix crystallizes (solidifies) on cooling to room temperature and the resultant bars are removed from the molds or the final mold acts as the package.

Bar Lather Test

- 10 The hand wash lather test is used to provide in-use lather volume measurements for the lather performance of skin cleansing bars. The test measures the lather volume generated under a soil load. Synthetic soil is used for the test reported herein. Its formula is reported in US 4,673,525 to Small et al. issued June 16th 1987, incorporated herein by reference.

Bar Hardness Test

- 15 1. The hardness of a bar is determined by measuring at 25°C the depth of penetration (in mm) into the bar of a 247 gram Standard Weighted Penetrometer Probe having a conical shaped needle attached to a 22.9 cm (9 inch) shaft weighing 47 grams with 200 grams on top of said shaft. A hardness measurement of 5 mm or less indicates a very hard bar; 5-12 mm indicates a moderately hard bar. This
20 defines "hardness" as used herein unless otherwise specified.

Bar Smear Test

- 25 2. The smear grade is determined by a (1) placing a soap bar on a perch in a 1400 mm diameter circular dish; (2) adding 200 ml of room temperature water to the dish such that the bottom 3 mm of the bar is submerged in water; (3) letting the bar soak overnight (15 hours); (4) turn the bar over and grade qualitatively for the combined amount of smear, and characteristics of smear, depth of smear on a scale where 10 equals no smear, 8.0-9.5 equals low smear amount, 5.0-7.5 equals moderate smears similar to most marketed bars, and 4.5 or less equals very poor smear.

- 30 Good Commercial soap bars, have smears of about 5 and 6, respectively.

THE EXAMPLES

The example bars are made using the above Batch Process unless otherwise specified.

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EXAMPLES A, B, & C

<u>Ingredients</u>	<u>A</u>	<u>B</u>	<u>C</u>
<u>Wt. %</u>	<u>Wt. %</u>	<u>Wt. %</u>	<u>Wt. %</u>
Sodium Myristic Soap (C14)	20.00	14.88	15.24
Myristic Free Fatty Acid (C14)		0.09	0.09
Sodium Lauric Soap (C12)		1.74	2.00
Lauric Free Fatty Acid (C12)		0.01	0.01
Coconut Soap		0.78	0.16
Coco Betaine	6.00		
Sodium Lauryl Sarcosinate	8.00		
Stearalkonium Chloride	3.00		
Perfume	0.50	0.50	0.50
Sodium Chloride	3.00	2.50	2.50
Petrolatum	15.00	12.80	12.80
Miscellaneous	0.86	1.21	3.47
Glycerine	15.00	5.00	5.50
Dimethicone		1.50	1.50
Sodium Cocoyl Isethionate		24.44	5.00
Sodium Isethionate		1.74	0.36
Cocoamidopropyl Hydroxysultaine		2.00	
Alkyl Glyceryl Ether Sulfonate			19.00
Mineral Oil		3.20	3.20
Water	28.64	27.61	28.67
Hardness (mm)	5.8	10.0	10.7
Smear	7.0	8.0	6.0
Lather	4.0	7.0	7.5
Consistency	1080-1345	354-430	354-430
G' at 1 Hz.	25M-40M	8500-9300	8500-9300
G'' at 1 Hz.	23.4M-36.4M	6700-7000	6700-7000
Overall User Acceptance Rating	47	68	68

* Mostly AGS by-products

Examples B and C are highly preferred examples. Example A has "overall user acceptance (100 is considered excellent and 0 poor)" much lower than Examples B and C.

5 Examples B and C are lipid blends containing petrolatum, mineral oil and silicone. Example A

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contains only petrolatum. Example A also gives skin feel impressions of being "very sticky", "greasy", "tacky feeling".

EXAMPLES D-G**EXAMPLES SHOWING USE OF DIFFERENT PREFERRED LIPIDS**

	D	E	F	G
<u>Ingredients</u>	<u>Wt. %</u>	<u>Wt. %</u>	<u>Wt. %</u>	<u>Wt. %</u>
Sodium Myristic Soap	20.00	20.00	20.00	20.00
Coco Betaine	6.00	6.00	6.00	6.00
Sodium Lauryl Sarcosinate	8.00	8.00	8.00	8.00
Stearylkonium Chloride	3.00	3.00	3.00	3.00
Perfume	0.50	0.50	0.50	0.50
Sodium Chloride	3.00	3.00	3.00	3.00
Glycerine	15.00	15.00	15.00	15.00
Petrolatum	12.00	13.65	12.00	15.00
Mineral Oil	3.00		3.00	
Cetyl Ricinoleate		3.00		
Dimethicone			3.00	
Isopropyl Palmitate			0.50	
Merquat 550 Polyquaternium 7			0.75	
JR 400 Polyquaternium 10			0.75	
Miscellaneous Minors	0.86	0.86	0.60	0.86
Water	28.64	28.64	25.40	28.64
Hardness)	--		6.8	8.9
Smear	8.0		8.5	7.0
Lather	2.5		3.0	4.0
Consistency, k	354-430		354-430	1080-1345
G' at 1Hz	8500-9300		8500-9300	25M-40M
G'' at 1Hz	6700-7000		6700-7000	23.4M-36.4M
LDV (range)	44.5			38-89

5

Examples D, E and F are preferred examples and use lipids blends selected from: Mineral oil, Isopropyl Palmitate, Cetyl Ricinoleate and Petrolatum. Example D is less sticky on the skin than Example G due to Example D's lower consistency k; even though they have comparable levels of Deposition.

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EXAMPLES H AND IEXAMPLES SHOWING USE OF DIFFERENT PREFERRED LIPID BLENDS

<u>Ingredients</u>	<u>H</u> <u>Wgt. %</u>	<u>I</u> <u>Wgt. %</u>
Sodium Myristic Soap (C14)	14.38	14.38
Coco Betaine		
Coconut Soap	0.62	0.62
Sodium Lauryl Sarcosinate		
Perfume- Odessa	0.50	0.50
Sodium Chloride	2.80	2.80
Petrolatum	14.40	14.40
Miscellaneous Minors	2.21	2.21
Glycerine	5.00	5.00
Sodium Cocoyl Isethionate	28.00	28.00
Sodium Isethionate	1.70	1.70
Octyl Isononanoate		3.60
Polydecene homopolymer	3.60	
Water	26.79	26.79
Hardness (mm)		
Smear		
Lather		
Consistency, k	283-292	
G' at 1Hz	5881-7160	
G'' at 1Hz	6118-6805	
LDV (range)		

- 5 Examples H and I use lipids blends selected from: Octyl Isononanoate, Polydecene and Petrolatum. These preferred lipid blends generally increase or maintain the slipperiness of the rinse while reducing the coated feel of pure petrolatum (Example G).

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EXAMPLES J-M

Ingredient	J	K	L	M
Myristic fatty Acid				
Sodium Myristic Soap			20	30
Sodium Palmitic Soap		19.9		
Palmitic Acid		.1		
Sodium Lauric Soap	19.9			
Lauric Acid	.1			
Coco Betaine	6	6	6	5
Sodium Lauryl Sarcosinate	8	8	8	7
Glycerine	15	15	15	13
NaCl	3	3	3	3
Perfume	0.5	0.5	0.5	0.5
Petrolatum	15	15	15	14
Miscellaneous.	0.86	.86	0.9	0.8
Water	28.64	28.64	29	24
Stearalkonium Chloride	3	3	3	3
Lather	1.5	0.5	2.5	3.5
Smear			9.0	8.5
Hardness.	6.47	9.23	6.4	4.8
LDV	136	12	42.5	4.5

Examples J, K and L are preferred bars. Different chain length soaps are used. Example J and L are more preferred than Example K, since Examples J and L have a soap fatty acid material with at least 25 % being C12 or C14. Examples L and M use of different levels of soap fatty acid material. All of these examples use a cationic surfactant: Stearalkonium Chloride, and Anionic Surfactants: Sodium Lauryl Sarcosinate and Coco Betaine

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EXAMPLES N-QLEVEL AND RATIO OF SOAP TO FATTY ACID MATERIAL

Series: Acid Soap

Ingredient	N	O	P	Q
Sodium Stearic Soap	10.5	15.49	5.47	3.74
Stearic Acid	10.5	5.16	.04	6.95
Sodium Myristic Soap	4.5		6.2	1.78
Myristic Acid	4.5		.05	3.30
Sodium Lauric Soap		6.75		0.05
Lauric Acid		2.25		0.09
Coconut Soap		.26	.73	
Coconut Fatty Acid		.09	.01	
Sodium Alkyl Isethionate.		16	23	21.60
Sodium Isethionate.		0.95	1.63	1.22
Coco Betaine	2			
Sodium Lauryl Sarcosinate	10.5			
Sodium Glycerylether Sulphonate				3.6
Cocoamidopropyl/Hydroxy Sultaine				1.08
Parrafin				3.6
Sodium Palmitic Soap				
Glycerine	15	6	7	16.4
NaCl	3	2	2.5	0.5
Perfume	0.5	0.5	.5	.3
Petrolatum	15	16	12.8	15.0
Mineral Oil			3.2	
Misc.	0.81	1.48	1.14	<2
Water	20.19	25.87	30.23	14.40
Stearalkonium Chloride	3	1.2		2.60
Ratio of Soap to fatty Acid	1:1	3:1	125:1	1:2
Level of Soap/Fatty Acid	30.0	30.0	12.5	15.9
Hardness.			FPB	FPB
LDV	6.72	20.7	47.3	8.8
Lipid Consistency	1080-1345	1080-1345	354-430	354-430

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Examples N, O, P and Q are preferred bars. Different soap to fatty acid ratios from 1:2 (Example Q) to 125:1 (Example P) are used. The total level of soap fatty acid material ranges from 12.5 to 30 parts.

5

EXAMPLES R-TLEVEL AND TYPE OF SYNTHETIC SURFACTANT

Series: Water / NaCl

Ingredient	R	S	T
Sodium Myristic Soap	20	20	15.34
Myristic Acid			.08
Sodium Lauric Soap			3.98
Lauric Acid			.02
Coconut Soap			.58
Sodium Cocoyl Isethionate.			18
Sodium Isethionate.			1.28
Coco Betaine	6	6.3	
Sodium Lauroyl Sarcosinate	8	14.4	
Glycerine	8	10.5	5
NaCl	5	3	3
Perfume	0.5	0.5	0.5
Petrolatum	15	15	13.6
Mineral Oil			3.4
Miscellaneous.	0.86	1.27	.89
Water	33.14	24.53	28.33
Stearalkonium Chloride	3	4.5	
Cocoamidopropyl/ Hydroxysultaine			6.0
Lather	3	2	
Smear	6		
Hardness.	9.67		11.3
Surfactant Level	14.0	25.2	24.0

Examples R, S and T are preferred bars, that use different anionic synthetic surfactants: Sodium Lauryl Sarcosinate, Sodium Isethionate; different amphoteric surfactants: Coco Betaine, Cocoamidopropyl HydroxySultaine, and a cationic surfactant (deposition aid): Stearalkonium Chloride, The total level of synthetic surfactant ranges from 17.0 parts to 25.2.

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EXAMPLES U, V AND WLEVEL AND TYPE OF DEPOSITION AIDS: POLYOLS AND CATIONIC SURFACTANTS

		<u>Preferred Bars</u>		
	<u>Ingredient</u>	U	V	W
5	Sodium Myristic Soap	20	20	20
	Sodium Lauroyl Sarcosinate	8	8	8
	Coco Betaine	6	6	6
	Sodium Chloride	3	3	3
	Glycerine	15	15	
10	Petrolatum	15	15	15
	Perfume	.5	.5	.5
	Stearalkonium Chloride	3		3
	Micellaneous	.9	.3	.9
	Water	29	32	44
15				
	Hardness (mm)	7.5	9.8	7.1
	Smear	8.5	7.0	8.0
	Lather	3.0	4.0	2.5
	LDV	62	10	16
20				

Examples U, V and W are preferred bars. Example U uses a highly preferred deposition aid polyol ingredient. Example U has 15 % Glycerine and deposits lipid at a significantly higher level than the non-polyol containing Example W. Example U also uses a second highly preferred deposition aid cationic surfactant ingredient. Example U has 3% Stearalkonium Chloride and deposits lipid at a significantly higher level than the non-cationic surfactant containing Example V.

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EXAMPLE X AND YFORMULAE TESTED VIA CRYO SEM SHOWING LIPID IN WATER EMULSION

<u>Ingredients</u>	<u>X</u>	<u>Y</u>
	<u>Wgt. %</u>	<u>Wgt. %</u>
Sodium Myristic Soap	20.00	11.5
Sodium Lauric Soap		2.9
Sodium Coconut Soap		0.6
Coco Betaine	6.00	
Sodium Lauryl Sarcosinate	8.00	
Sodium Cocoyl Isethionate		28.0
Stearyl Dimethyl Benzyl Ammonium Chloride	3.00	
Perfume	0.50	0.50
Sodium Chloride	3.00	3.00
Sodium Isethionate		1.7
Glycerine	15.00	5.00
Petrolatum	15.00	14.40
Mineral Oil		3.60
Miscellaneous Minors	0.86	2
Water	28.64	26.80

Examples X and Y are preferred bars analyzed via Cryo SEM and are shown in the Figures.

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EXAMPLES Z-CCLEVEL AND TYPE OF THE HIGHLY PREFERRED OPTIONAL POLYOL

Series: Solvent

Ingredient	Z	AA	BB	CC
Sodium Myristic Soap	17.91	17.2	15.89	15.89
Myristic Acid	.09	.09	.09	.09
Sodium Lauric Soap	1.99	1.99	1.84	1.84
Lauric Acid	.01	.01	.01	.01
Coconut Soap		.71	.67	.67
Sodium Cocoyl Isethionate.		22	21	21
Sodium Isethionate.		1.56	1.56	1.56
Sorbitol	7	5.5		
Alkyl Glyceryl Ether/ Sulfonate	20			
Propylene Glycol			3	6
Glycerine			5.1	2.1
NaCl	2.5	2	2.2	2.2
Perfume	0.5	0.5	0.5	.05
Petrolatum	13.6	12.8	12.8	12.8
Mineral Oil	3.4	3.2	3.2	3.2
Miscellaneous.	4.03	1.6	1.04	1.04
Water	26.67	26.24	27	27
Dimethicone	1.5	1.5	1.5	1.5
Merquatt 550 Polymer	0.8	0.8	0.8	0.8
Coco Hydroxy Sultaine		1.3	1.8	1.8
Hardness.	8.3	10.1		
LDV	78	142	188	35

Examples Z, AA, BB and CC are highly preferred bars, and use different types of the
5 highly preferred optional ingredients (deposition aid): propylene glycol, sorbitol and glycerine.

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EXAMPLES DD-FF

Ingredient	<u>LIPID LEVEL</u>		
	DD	EE	FF
Sodium Myristic Soap	20	20	20
Myristic Acid			
Coco Betaine	6	6	6
Sodium Lauryl Sarcosinate	8	8	8
Glycerine	18.5	15	13.4
NaCl	3	3	3
Perfume	0.5	0.5	0.5
Petrolatum	10	15	20
Mineral Oil			
Miscellaneous	.6	.8	.6
Water	31.9	28.7	27
Dimethicone			
Stearalkonium Chloride	1.5		1.5
Behenyl Trimethyl/ Ammonium Chloride		3.0	
Lather	3.5	3.0	3.5
Smear	8	7.5	7.5
LDV	1.99	41	43.2
Lipid Consistency	1080-1345	1080-1345	1080-1345

5 Examples EE and FF are preferred bars. Example DD has a lower deposition than preferred. These use different levels of lipid from 10 to 30 parts. Example EE contains 3.0 % of a highly preferred cationic surfactant (deposition aid): Behenyl Trimethyl Ammonium Chloride.

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EXAMPLES GG-JJLEVEL, TYPE AND RATIO OF ANIONIC SYNTHETIC SURFACTANTS

	<u>Ingredient</u>	GG	HH	II	JJ
5	Sodium Myristic Soap	20	20	20	20
	Sodium Lauroyl Sarcosinate	8		14	14
	Coco Betaine				6
	Alkyl glyceryl Sulfonate	6			
	Sodium Cocoyl Isethionate		12.0		
10	Sodium Lauroyl Isethionate		2.0		
	Sodium Chloride	3	3	3	3
	Glycerine	15	15	15	15
	Petrolatum	15	15	15	15
	Perfume	0.5	0.5	0.5	0.5
15	Stearalkonium chloride	3	3	3	3
	Micellaneous	<2	<2	<2	<2
	Water	28	28	28	23
20	Hardness (mm)	10.5	11.1	9.3	8.5
	Smear	8.5	6.0	9.0	6.5
	Lather	2.0	3.0	1.0	3.5
	LDV	22	7	56	72

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EXAMPLES KK AND LLGELLING AGENTS, USED TO MODIFY LIPID RHEOLOGY

	<u>Ingredient</u>	<u>KK</u>	<u>LL</u>
	Sodium Myristic Soap	19.22	19.10
5	Sodium Lauric Soap	.39	
	Na coconut Soap	.39	
	Sodium Lauroyl Sarcosinate	12.00	
	Sodium cocooyl isethionate	12.00	28.00
	Sodium Chloride	2.00	2.80
10	Glycerine	10.00	5.00
	Petrolatum	8.30	
	*Polydecene gel	8.30	
	Polydecene		18.00
	Misc	< 2	<2
15	Water	25.09	27.07
	LDV	68	9

*Polydecene gel consists of 17.3 % sucrose polyester, 69.6 % polydecene, 12.9 % polyethylene polymer gellant.

Examples KK and LL are highly preferred bars, and highlight the use of different lipid types and specifically the use of oil thickening polymers, such as polyethylene to modify the rheological properties of the lipid.

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EXAMPLE MMCOMPARATIVE EXAMPLE

<u>Ingredients</u>	<u>MM</u> <u>Wgt. %</u>
Sodium Myristic Soap	28.00
Magnesium Myristic Soap	5.00
Myristic fatty Acid	0.50
Coco Betaine	10.00
Sodium Lauryl Sarcosinate	3.00
Perfume	0.50
Sodium Chloride	2.58
Propylene Glycol	3.50
Petrolatum	22.50
Miscellaneous Minors	0.84
Water	24.44

- Comparative Example MM is made by a freezer process as disclosed in allowed US Pat.
- 5 Application Serial No. 07/782,956 to Kacher et al., filed 11/01/91, and 08/037,479, Taneri et al., 03/24/93, both incorporated herein by reference. It has a rigid crystalline structure, but deposits less than 3 μ g of lipid per sq cm of skin tested using Lipid Deposition Protocol 1.

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EXAMPLE NN

NN	
<u>Ingredients</u>	<u>Wgt. %</u>
Sodium Myristic Soap	15.78
Myristic Fatty Acid	0.09
Sodium Lauric Soap	1.84
Lauric Fatty Acid	0.01
Coconut Soap	0.78
Sodium Coco Isethionate	24.44
Sodium Isethionate	1.74
Cocoamidopropyl Hydroxysultaine	2.00
Perfume	0.50
Sodium Chloride	2.50
Glycerine	5.00
Petrolatum	14.40
Mineral Oil	1.60
Miscellaneous Minors	1.21
Water	28.11
Hardness	9.50
Smear	5.5
Lather	7.5
LDV	50.5

Example NN is a highly preferred bar made by an In-Line Mixing Process as described above.

5 **WHAT IS CLAIMED IS:**

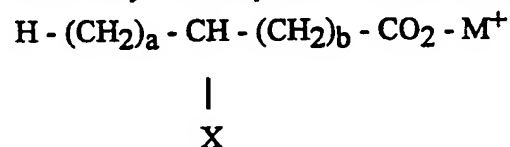
What is claimed is:

Claim 1. A lathering skin cleansing bar composition comprising by *weight parts of the bar composition*:

- (a) from about 5 parts to about 40 parts of a lipid skin moisturizing agent, selected from the group of organic lipids, which are hydrophobic as defined by having a combined Vaughan Solubility Parameter (VSP) of from about 5 to less than about 10; and mixtures thereof;
- (b) from about 10 parts to about 50 parts of a rigid semi-continuous, interlocking open mesh crystalline network structure consisting essentially of a fatty acid soap material selected from the group consisting of fatty acid soap has AT LEAST 75 % saturated alkyl chains; said alkyl chains being selected from the group consisting of chains of from 8 to 22 carbon atoms, and mixtures thereof; and;
- (c) from about 1 part to about 50 parts of a lathering synthetic surfactant; and
- (d) from about 10 parts to about 50 parts water;

wherein said water and said lipid are predominantly within interstices of said open mesh crystalline network; wherein said bar composition has a Lipid Deposition Value of at least 3 to about 1000..

Claim 2. The lathering skin cleansing bar composition of Claim 1 wherein at least 80 % of said fatty acid soap material has the following structure:



wherein:

$$a + b = 8 \text{ to } 20$$

$$\text{each } a, b = 0 \text{ to } 20$$

X = H, OR, O-CO-R, R, or mixtures thereof

R = C1-C3 alkyl, H, or mixtures thereof

M = Na, (1/2Mg), or mixtures thereof; and;

wherein said fatty acid soap material comprises 15 to 40 parts by *weight of the bar composition*; and wherein said fatty acid soap material has at least 85 % saturated alkyl chains; and wherein about 80 % to 100 % of said saturated alkyl chains are selected from the group consisting of 12 to 18 carbon atoms chains; and wherein said soap and said fatty acid have a ratio of from 1:3 to 10,000:1; and wherein said lipid is about 10 to 40 parts by *weight of the bar composition*; wherein said lipid has a viscosity

consistency k value of 5 poise to 5,000 poise at 35 C; and wherein said lipid has a shear index at 35°C in the range 0.1 to 0.8.

Claim 3. The lathering skin cleansing bar composition of Claim 2; wherein said lathering synthetic surfactant is from 5 to 40 parts by *weight of the bar composition*; and wherein said lathering synthetic surfactant is selected from the group consisting of anionic surfactants; nonionic surfactants, amphoteric surfactants, and mixtures thereof; and wherein said lathering synthetic surfactant has a critical micelle concentration (CMC) equilibrium surface tension value of from 15 to 50 dynes per cm at 25°C; and said water is 15 to 45 parts; and wherein said lipid is from about 10 to 35 parts by *weight of the bar composition*; and, wherein said lipid is selected from the group consisting of: hydrocarbon oils and waxes, silicone oils, di and tri-glyceride fats and oils, acetoglyceride esters, alkyl esters, alkenyl esters, polyol fatty acid polyesters, lanolin and its derivatives, wax esters, beeswax derivatives, vegetable waxes, sterols and phospholipids; and wherein said bar has a Lipid Deposition Value of 5 to 500;

and wherein;

said hydrocarbon oil and wax is **preferably** selected from the group consisting: petrolatum, mineral oil micro-crystalline waxes, polyalkenes, paraffin, cerasin, ozokerite, polyethylene and perhydrosqualene;

said silicone oil is **preferably** selected from the group consisting: dimethicones, cyclomethicones, alkyl siloxanes, polymethylsiloxanes and methylphenylpolysiloxanes;

said di and tri glyceride is **preferably** selected from the group consisting: hydroxylated milk glyceride, castor oil, soy bean oil, maleated soy bean oil, safflower oil, cotton seed oil, corn oil, walnut oil, peanut oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil and sesame oil;

said alkyl ester is **preferably** selected from the group consisting: isopropyl esters of fatty acids and alkyl esters of riconoic acid isopropyl palmitate, isopropyl myristate, cetyl riconoleate and stearyl riconoleate; hexyl laurate, isohexyl laurate, myristyl myristate, isohexyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, diisopropyl adipate, diisohexyl adipate, dihexyldecyl adipate, diisopropyl sebacate, acyl isononanoate lauryl lactate, myristyl lactate, oleyl myristate, oleyl stearate and oleyl oleate. and cetyl lactate;

said lanolin based material is **preferably** selected from the group consisting: lanolin oil, lanolin wax, lanolin alcohol, lanolin fatty acid, isopropyl lanolate, acetylated

lanolin, acetylated lanolin alcohols, lanolin alcohol linoleate, lanolin alcohol riconoleate;

said wax esters is **preferably** selected from the group consisting: beeswax and beeswax derivatives, spermaceti, myristyl myristate, stearyl stearate;

said vegetable wax is **preferably** selected from the group consisting carnauba and candelilla waxes;

said sterol is **preferably** selected from the group consisting: cholesterol, cholesterol fatty acid esters and homologs thereof;

said phospholipid is **preferably** selected from the group consisting: lecithin and derivatives, Sphingo lipids, ceramides, glycosphingo lipids; and homologs thereof; and mixtures thereof;

and wherein said lipid is **preferably** from about 10 parts to about 30 parts, by weight of the bar composition; and wherein said bar has a Lipid Deposition Value in the range 10 to 500; and wherein **preferably** at least 70 % of said lipid phase is composed of lipids selected from the group consisting: petrolatum, mineral oil micro-crystalline waxes, polyalkenes, paraffin, cerasin, ozokerite, polyethylene and perhydrosqualene; dimethicones, cyclomethicones, alkyl siloxanes, polymethylsiloxanes and methylphenylpolysiloxanes, hydroxylated milk glyceride, castor oil, soy bean oil, maleated soy bean oil, safflower oil, cotton seed oil, corn oil, walnut oil, peanut oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil and sesame oil; lanolin, lanolin oil, lanolin wax, lanolin alcohol, lanolin fatty acid, isopropyl lanolate, acetylated lanolin, acetylated lanolin alcohols, lanolin alcohol linoleate, lanolin alcohol riconoleate; and mixtures thereof.

Claim 4. The lathering skin cleansing bar composition of Claim 2 wherein said fatty acid soap material comprises 15 to 40 parts by *weight of the bar composition*; and wherein said fatty acid soap material has at least 85 % saturated alkyl chains; and wherein 80 % to 100 % of said saturated alkyl chains are selected from the group consisting of 12 to 18 carbon atoms chains; wherein said composition contains some free fatty acid and wherein said soap to said free fatty acid ratio is from about 2:1 to about 200:1; and wherein said lipid is 10 to 40 parts by *weight of the bar composition*; and wherein said lipid has a viscosity k value of 5 poise to 5,000 poise at 35 C;

and wherein;

said anionic synthetic surfactant parts is from about 3 to about 35 parts, and wherein said lathering anionic synthetic surfactant is selected from the group consisting: acyl isethionates, acyl sarcosinates, alkylglycerylether sulfonates, methylacyl taurates, paraffin sulfonates, linear alkyl benzene sulfonates, N-acyl glutamates, alkyl sulfosuccinates, alpha sulfo fatty acid esters, alkyl ether carboxylates, alkyl phosphate esters, ethoxylated alkyl phosphate esters, alkyl amine oxides, alpha olefin sulphates, the alkyl ether sulfates (with 1 to 12 ethoxy groups), and mixtures thereof, wherein said surfactants contain C8 to C22 alkyl chains and wherein the counterion is selected from the group consisting of : Na, K, NH_4 , $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$.

Claim 5. The lathering skin cleansing bar composition of Claim 4 wherein the fatty acid material parts is from about 15 parts to about 35 parts; wherein at least 25 % of the fatty acid soap material have alkyl chains of 12 to 14 carbon atoms, wherein at least 95 % of said alkyl chains are saturated; and wherein said soap is at least four times said fatty acid; and wherein said fatty acid soap is selected from a group consists of at least 75 % sodium soap; and wherein said lipid parts is from about 12 parts to about 24 parts by weight of the bar; wherein the said bar has a Lipid Deposition Value of 25 to 500; and wherein said water parts is from about 15 to about 35 parts, by weight;

and wherein said anionic surfactant is **preferably** from about 8 to about 30 parts selected from the group consisting of acyl isethionate, acyl sarcosinates, alkyl sulfosuccinates, alkylglycerylether sulfonates, methylacyl taurates, alkyl ether sulfates, alkyl sulfates, alkyl phosphate esters and mixtures thereof, wherein said surfactants contain C8 to C18 alkyl chains; and wherein the counterion is Na; and wherein said amphoteric synthetic surfactant is **preferably** from about 1 to about 10 parts selected from the group consisting: alkyl-ampho mono- and di- acetates, alkyl betaines, alkyl sultaines, alkyl amidopropyl betaines, alkyl amidopropyl hydroxysultaines, and mixtures thereof, wherein said amphoteric surfactant contain C12 to C22 alkyl chains; and wherein said lathering synthetic surfactant has a critical micelle concentration (CMC) equilibrium surface tension value of from 15 to 45 dynes per cm; and wherein said lathering synthetic surfactant parts is **preferably** from about 10 to about 35 parts, by weight; and is **preferably** selected from the group consisting of: anionic and/or amphoteric synthetic surfactant and wherein said anionic surfactant is more **preferably** selected from the group consisting of sodium lauryl and coco isethionate, sodium lauryl and coco sarcosinates, sodium C12-C16 sulfosuccinates, sodium C12-16 alkylglycerylether sulfonates, sodium lauryl and coco taurates; and wherein said

amphoteric surfactant is **preferably** selected from the group consisting: lauryl and coco betaines, lauryl and coco hydroxy sultaines, and mixtures thereof; and wherein ratio of said anionic to amphoteric is **preferably** from about 1:1 to about 30:1.

Claim 6. The lathering skin cleansing bar composition of Claim 5, wherein said synthetic surfactant parts comprises from about 3 to about 17 parts of a nonionic lathering synthetic surfactant selected from the group consisting: alkyl glucose amides, alkyl glucose esters, polyoxyethylene amides, fatty alkane amides, alkyl amine oxides, alkyl polyglucosides, polyoxy ethylene alkyl phenols, polyoxyethylene esters of fatty acids, EO/PO block co-polymers such as polyoxamines and poloxamers, sorbitan esters and alcohol esters, and mixtures thereof.

Claim 7. A lathering skin cleansing bar composition comprising by *weight parts of the bar composition*:

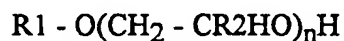
- (a) from about 5 parts to about 40 parts of a lipid skin moisturizing agent, selected from the group of organic lipids, which are hydrophobic as defined by having a Vaughan Solubility Parameter (VSP) of from about 5 to less than about 10; and mixtures thereof;
- (b) from about 10 parts to about 50 parts of a rigid semi-continuous, interlocking open mesh crystalline network structure consisting essentially of a fatty acid soap material selected from the group consisting of fatty acid soap has at least 75% saturated alkyl chains; said alkyl chains being selected from the group consisting of chains of from 8 to 22 carbon atoms, and mixtures thereof; and;
- (c) from about 1 part to about 50 parts of a lathering synthetic surfactant; and
- (d) from about 10 parts to about 50 parts water;
- (e) from about 0.5 to about to about 6 parts of a cationic surfactant; and

wherein said water and said lipid are predominantly within interstices of said open mesh crystalline network; wherein said bar composition has a Lipid Deposition Value of at least 3 to about 1000; and wherein said cationic surfactant improves the Lipid Deposition Value; and wherein said cationic synthetic surfactant parts is **preferably** from about 0.5 to about 6 parts, by weight of the composition, and wherein said cationic synthetic surfactant is **preferably** selected from the group consisting: alkyl-trimonium chloride and methyl sulphate, alkyl trimonium chloride and methyl sulphate, alkyl alkonium chloride and methyl sulphate, and di-alkyl dimonium chloride and methyl sulphate, and mixtures thereof, wherein said cationic surfactant **preferably** contain C12 to C24 carbon atoms per alkyl chain; and wherein said cationic surfactant

is more preferably selected from the group consisting of stearalkonium chloride, stearyltrimonium chloride, Di-stearyl-dimonium chloride, and mixtures thereof.

Claim 8. A lathering skin cleansing bar composition comprising by *weight parts of the bar composition*:

- (a) from about 5 parts to about 40 parts of a lipid skin moisturizing agent, selected from the group of organic lipids, which are hydrophobic as defined by having a Vaughan Solubility Parameter (VSP) of from about 5 to less than about 10; and mixtures thereof;
- (b) from about 10 parts to about 50 parts of a rigid semi-continuous, interlocking open mesh crystalline network structure consisting essentially of a fatty acid soap material selected from the group consisting of fatty acid soap has at least 75% saturated alkyl chains; said alkyl chains being selected from the group consisting of chains of from 8 to 22 carbon atoms, and mixtures thereof; and;
- (c) from about 1 part to about 50 parts of a lathering synthetic surfactant; and
- (d) from about 10 parts to about 50 parts water;
- (e) from about 0.5 to about 35 parts water soluble, organic material is selected from the group consisting of a polyol of the structure:



where R1 = H, C1-C4 alkyl; R2 = H, CH₃ and n = 1 - 200; C2-C10 alkane diols; guanidine; glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium); lactic acid and lactate salts (e.g., ammonium and quaternary alkyl ammonium); polyhydroxy alcohols such as sorbitol, glycerol, hexanetriol, propylene glycol, hexylene glycol and the like; polyethylene glycol; sugars and starches; sugar and starch derivatives (e.g. alkoxylated glucose); panthenol (including D-, L-, and the D,L- forms); pyrrolidone carboxylic acid; hyaluronic acid; lactamide monoethanolamine; acetamide monoethanolamine; urea; and ethanol amines of the general structure (HOCH₂CH₂)_xNH_y where x = 1-3; y = 0-2, and x+y = 3, and mixtures thereof; wherein said bar contains a non-volatile, organic material having a solubility of a least 50 % in water; and wherein said water soluble organic material at least 50 % soluble in water; and wherein said water and said lipid are predominantly within interstices of said open mesh crystalline network; wherein said bar composition has a Lipid Deposition Value of at least 3 to about 1000.

Claim 9. The lathering skin cleansing bar composition of Claim 8 wherein said water soluble organic material parts is from about 3 to about 20 parts, by weight said bar; and wherein said organic material is selected from the group consisting of glycerine, polyoxypropylene (1) glycerol and polyoxypropylene (3) glycerol, sorbitol, butylene glycol, propylene glycol, sucrose, and urea and triethanolamine; and mixtures thereof; and wherein said lipid is from about 15 parts to about 25 parts, by weight of the bar; and wherein said synthetic surfactant is from about 15 to about 30 parts by weight of the bar; said soap is present at a level from about 15 parts to about 25 parts and said soap is essentially C-12-18 carboxylic acids, with at least 50 % being C12 or C14; and wherein at least 75 % of said lipid by weight of said lipid is selected from the group consisting: petrolatum, micro crystalline wax, mineral oil or polydecene and mixes thereof; and wherein 0 to 25 % of said lipid by weight of said lipid is selected from the group consisting: dimethicone or alkyl polysiloxane and mixtures thereof; and wherein said water is preferably present at a level from about 15 parts to about 35 parts; and wherein said lipid parts is preferably from about 15 to 25 parts, by weight of the composition at least 75 % of said lipid is selected from the group consisting: petrolatum, micro crystalline wax, mineral oil or polydecene; and wherein said lipid has an elastic modulus (G') measured at 1 Hz. and 35°C in the range 1,000 to 80,000 dynes/sq. cm and has a viscous modulus (G'') measured at 1 Hz. and 35°C in the range 500 to 300,000 dynes/ sq. cm.; and wherein said bar contains from about 0.1 parts to about 10 parts of a polymeric, nonionic, cationic or hydrophobically modified polymeric skin feel aid, selected from the group consisting of cationic polysaccharides of the cationic guar gum class with molecular weights of 1,000 to 3,000,000, cationic and nonionic homopolymers derived from acrylic and/or methacrylic acid, cationic and nonionic cellulose resins; cationic copolymers of dimethyldialkylammonium chloride and acrylic acid; cationic homopolymers of dimethyldialkylammonium chloride; cationic polyalkylene and ethoxypolyalkylene imines; and mixes thereof; and wherein said polymeric, nonionic or cationic polymeric skin feel aid parts is preferably from about 0.25 parts to about 3 parts, by weight, and is preferably selected from the following group consisting: hydroxypropyl guar, guar hydroxypropyltrimonium chloride, polyquaternary 3, 5, 6, 7, 10, 11 and 24 and mixes thereof.

Claim 10. A lathering skin cleansing bar composition comprising by *weight parts of the bar composition*:

- (a) from about 5 parts to about 40 parts of a lipid skin moisturizing agent, selected from the group of organic lipids, which are hydrophobic as defined by having a

Vaughan Solubility Parameter (VSP) of from about 5 to less than about 10; and mixtures thereof;

- (b) from about 10 parts to about 50 parts of a rigid semi-continuous, interlocking open mesh crystalline network structure consisting essentially of a fatty acid soap material selected from the group consisting of fatty acid soap has AT LEAST 75 % saturated alkyl chains; said alkyl chains being selected from the group consisting of chains of from 8 to 22 carbon atoms, and mixtures thereof; and;
- (c) from about 1 part to about 50 parts of a lathering synthetic surfactant; and
- (d) from about 10 parts to about 50 parts water;

wherein said water and said lipid are predominantly within interstices of said open mesh crystalline network; wherein said bar composition has a Lipid Deposition Value of at least 3 to about 1000, and .

wherein said bar contains from about 0.1 parts to about 50 parts of other ingredients selected from the group consisting of:

from about 0.5 to about 5 parts potassium soap;

from about 0.5 to about 5 parts alkoxylated ammonium and/or alkylammonium and/or alkoxylated aliphatic amines and/or polyethoxylated amine soap;

from about 0.5 to about 15 parts calcium soap;

from about 0.5 to about 50 parts of impalpable water insoluble materials selected from the group consisting of calcium carbonate and talc;

from about 0.5 to about 25 parts of aluminosilicate clay and/or other clays; wherein said aluminosilicates and clays are selected from the group consisting of zeolites, kaolin, kaolinite, bentonite, halloysite, calcined clays, montmorillonite, illite and attapulgite.

from about 0.5 to about 25 parts dextrin, corn and wheat starch;

from about 0.1 to about 15 parts of salt and salt hydrates; and mixtures thereof; and wherein said salt and salt hydrate have a cation selected from the group consisting of: sodium, potassium, magnesium, calcium, aluminum, lithium ammonium, alkoxylated ammonium, alkylammonium, alkoxylated aliphatic amines, polyethoxylated amines; and wherein said salt and/or salt hydrate have an anion selected from the group consisting of: chloride, sulfate, isethionate, bromide, metasilicate, orthophosphate, pyrophosphate, polyphosphate, metaborate, tetraborate, carbonate, bicarbonate, hydrogen phosphate, methyl sulfate, and mono- and polycarboxylate of 1 to 6 carbon atoms or less;

from about 0.1 to about 1 parts whitening aid;

from about 0.1 to about 2 parts of a fragrance or perfume;

from about 0.1 to about 5 parts of a chelant, preserve or anti fungal/anti microbial/bacterial agent.

Claim 11. A lathering skin cleansing bar composition comprising *by weight parts of the bar composition*:

- (a) from about 5 parts to about 40 parts of a lipid skin moisturizing agent, selected from the group of organic lipids, which are hydrophobic as defined by having a Vaughan Solubility Parameter (VSP) of from about 5 to less than about 10; and mixtures thereof;
- (b) from about 10 parts to about 50 parts of a rigid semi-continuous, interlocking open mesh crystalline network structure consisting essentially of mixtures of mono and di-carboxylic fatty acid soap material selected from the group consisting of mono and di-carboxylic fatty acid soap and mixtures of said soap and mono and di carboxylic fatty acid; wherein said fatty acid soap material has AT LEAST 75 % saturated alkyl chains; said alkyl chains being selected from the group consisting of chains of from 8 to 22 carbon atoms, and mixtures thereof; and wherein said soap and said fatty acid have a ratio of from 1:3 to 10,000:1;
- (c) from about 1 part to about 50 parts of a lathering synthetic surfactant; and
- (d) from about 10 parts to about 50 parts water;

wherein said water and said lipid are predominantly within interstices of said open mesh crystalline network; wherein said bar composition has a Lipid Deposition Value of at least 3 to about 1000.

Claim 12. The lathering skin cleansing bar composition of Claim 1, wherein said lipid has a shear index at 35°C in the range 0.1 to 0.5 and a consistency k at 35°C in the range 10 to 3,000 poise; and wherein said lipid preferably has an elastic modulus (G') measured at 1Hz and 35°C in the range 25 to 100,000 dynes/sq. cm and has an viscous modulus (G'') measured at 1Hz and 35 C in the range 25 to 500,000 dynes/ sq. cm.; and wherein said elastic modulus (G') is more preferably in the range of 5,000 to 50,000 dynes/sq. cm and has a viscous modulus (G'') in the range of 5,000 to 100,000 dynes/ sq. cm.

Claim 13. The lathering skin cleansing bar composition of Claim 2, wherein said lipid is from about 12 parts to about 25 parts, by weight of the bar composition; and wherein said lipid has a k value of 50 to 2000 poise; and wherein at least 70 % of said lipid is composed of lipids selected from the group consisting: petrolatum, mineral oil, micro crystalline wax, paraffin, polyethylene, polybutene, polydecene, dimethicones, alkyl siloxane, cyclomethicones, lanolin, lanolin oil, lanolin wax; with the remainder

selected from: isopropyl palmitate, cetyl riconoleate, octyl isononanoate, octyl palmitate, isocetyl stearate, hydroxylated milk glyceride; and mixtures thereof, and wherein said water forms an aqueous phase, wherein, 20 to 95 % of said aqueous phase is water; and wherein the ratio of said water to said lipid parts is preferably greater than 1:1; and wherein said water is 15 to 35 parts; and wherein said aqueous phase and said lipid form a lipid in water emulsion entrapped in said interlocking open mesh crystalline network; and wherein said bar produces an unstable lipid in water emulsion when subjected to Lipid Stability Centrifuge Test.

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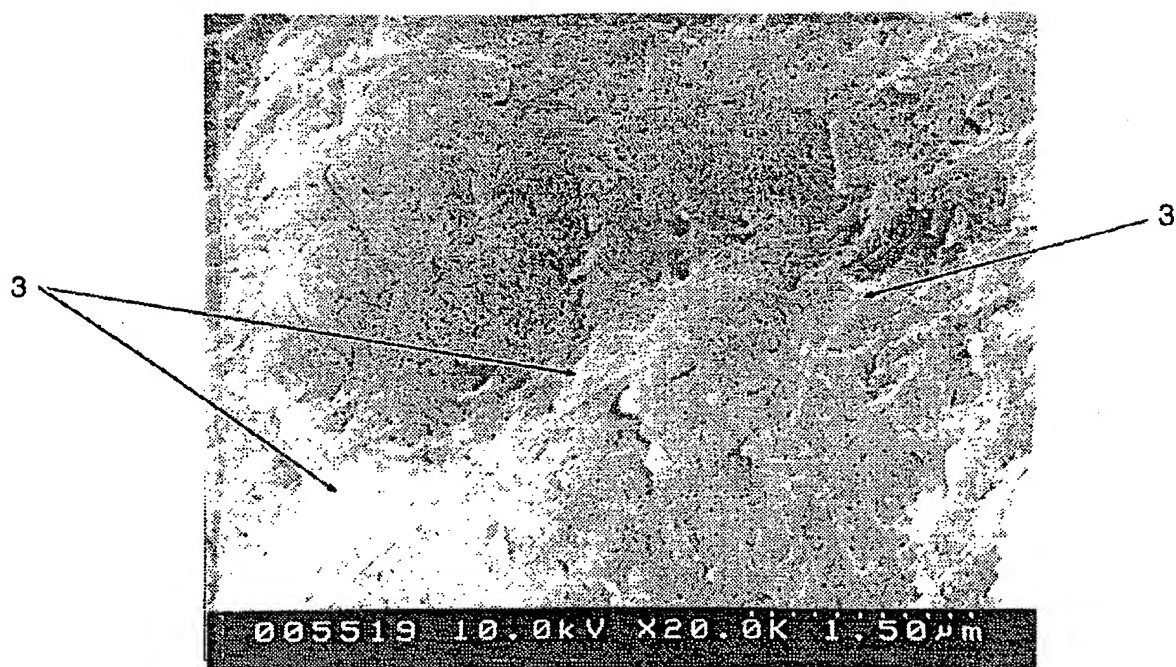


Fig. 1

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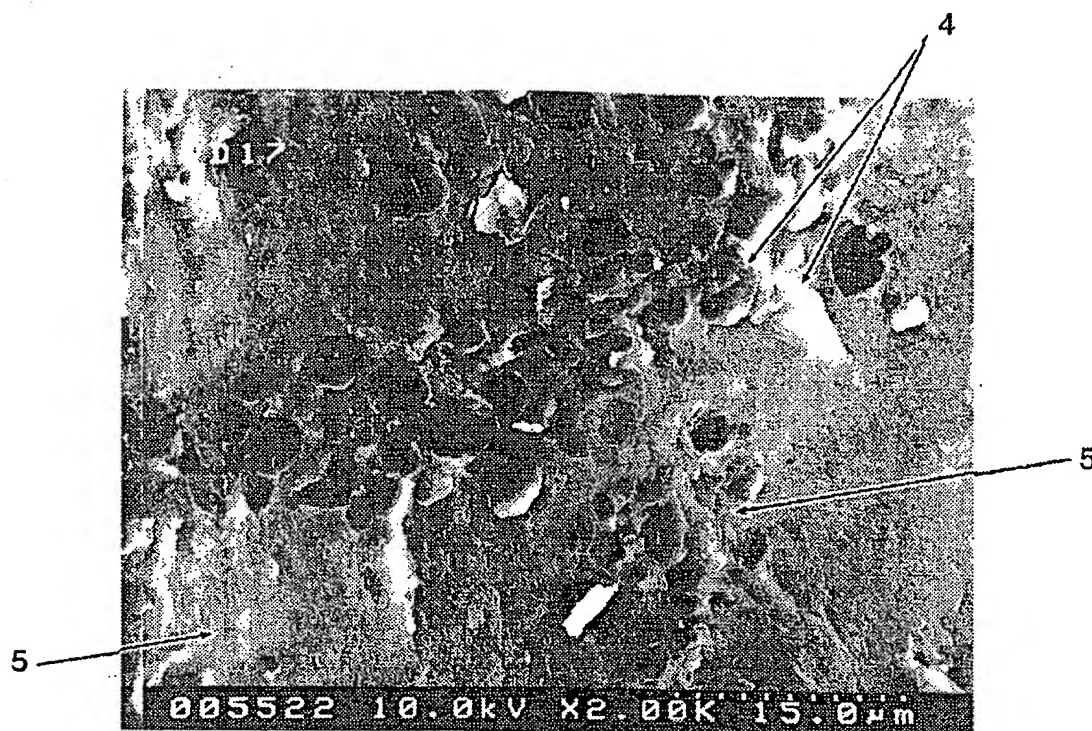


Fig. 2

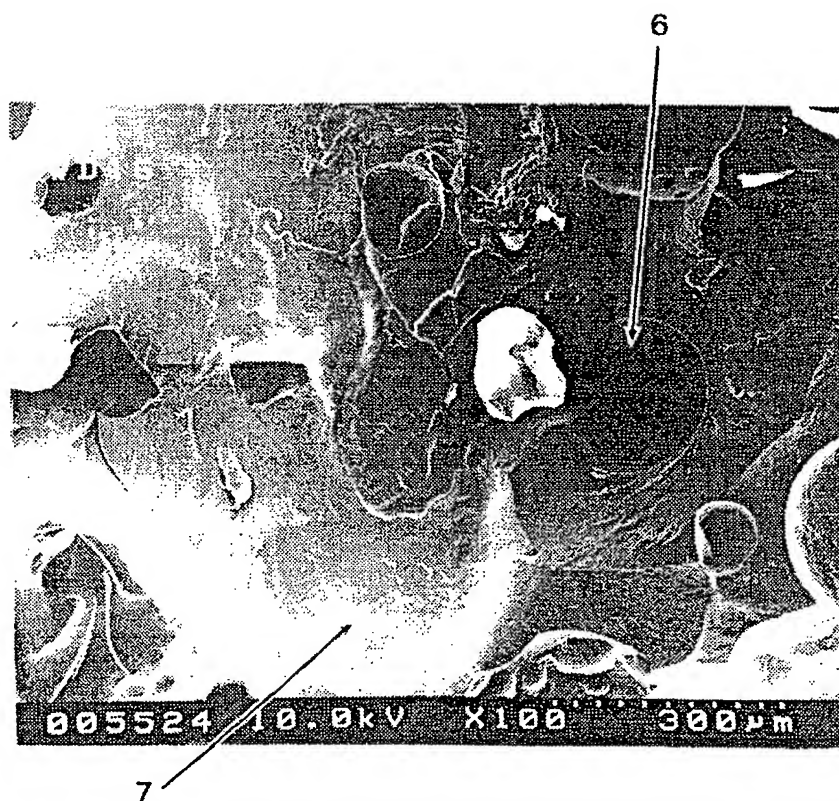


Fig. 3

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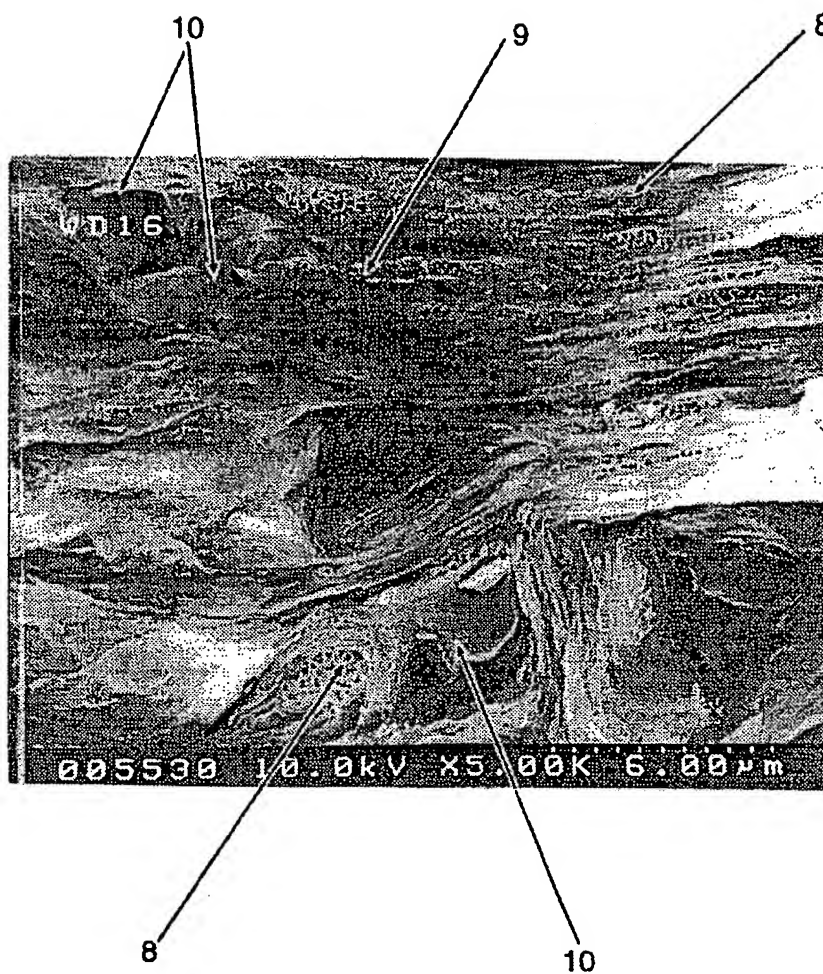


Fig. 4

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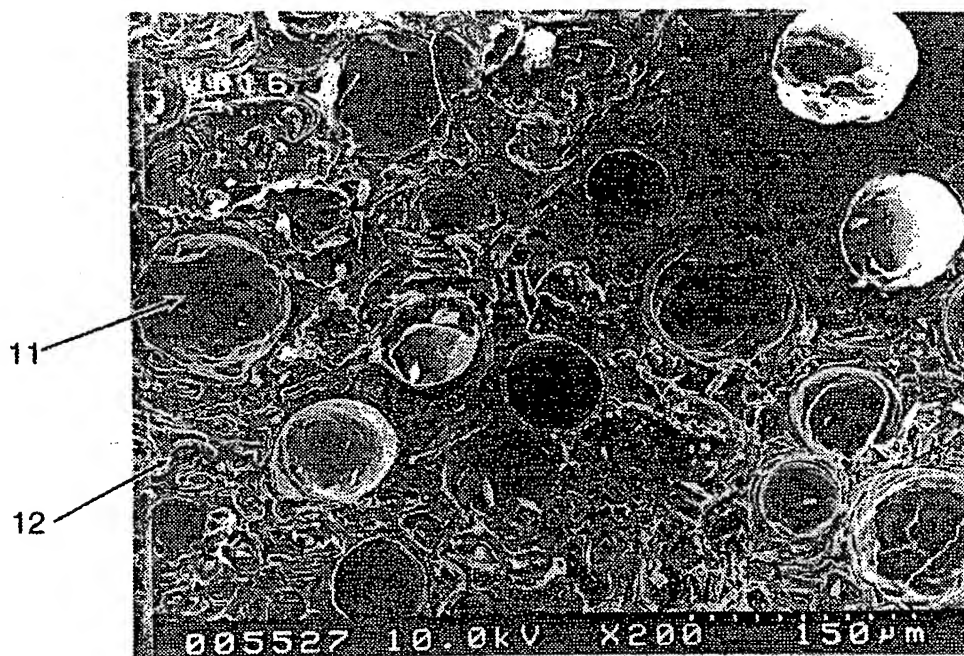


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US 95/02588

A. CLASSIFICATION OF SUBJECT MATTER

A 61 K 7/50

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A 61 K, C 11 D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5 262 079 (M.L. KACHER et al.) 16 November 1993 (16.11.93), the whole document. --	1-13
A	EP, A, 0 308 190 (THE PROCTER & GAMBLE COMPANY) 22 March 1989 (22.03.89), claims. --	1-13
A	US, A, 4 812 253 (L.E. SMALL et al.) 14 March 1989 (14.03.89), claims (cited in the application). ----	1-13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search
16 June 1995

Date of mailing of the international search report

25. 07. 95

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ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office.

In Recherchenbericht geführtes Patentedokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication		Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets		Datum der Veröffentlichung Publication date Date de publication	
JP A	5262079	16-11-93		AU CA EP FI HU NO NO WO	A1 A1 A1 A0 A0 A0 A0 A1	381444/93 107823/93 663161/93 944444/93 944444/93 940022/99 940022/99 940022/99 931915/94	21-10-93 10-11-93 04-01-94 14-09-94 14-09-94 03-08-99 03-08-99 03-08-99 00-09-93
EP A2	308190	22-03-89		AT AU AU CA CA DE DE FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR FR			

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